Abbreviations

Polymer I	Poly triethanylamineglyceryl-maleat (25:75%)
polmerII	Poly triethanylamineglyceryl-maleat (50:50%)
Polymer III	Poly triethanylamine-maleat
PPV	Poly(phenylen vinylen)
Polyani	Poly aniline
IR	Infra red
E°	Standard electrode potential
$\acute{\varepsilon}$	Dielectric constant
F.T.IR	Fourier transform infra red
U	Drop in potential
I	Current
R	Resistance
Ω	Ohm (Resistance unit)
NMR	Nuclear magnetic resonance
ρ	Resistivity
σ	Conductivity
μ	Mobility
e	Electron charge
T_c	Critical temperature
σ_v	Volume conductivity
$S \equiv \Omega^{-1}$	Siemens≡mho(conductance unit)
R^{-1}	conductance
VB	Valance Band
CB	Conduction Band

PPS	**Polyphenylen sulphide**
ρ_v	**Volume resistivitty**
A	**Gared electrode effective area**

Acknowledgement

Above all else, I want to express my great thanks to ALLAH for the uncountable gifts and for helping me to present this thesis.

The honor is mine to express my sincere thanks and gratitude to my supervisor Dr.Emad Taha Bakir for his guidance and sustained efforts throughout this work.

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Mustafa 2007

الخلاصة

ضمن مجال هذه الدراسة تم تحضير بوليمر متشابك بثلاثة نسب مختلفة هي (٢٥:٧٥%)،(٥٠:٥٠%)و (١٠٠:٠%)(كليسيرول:تراي ايثانول امين)وهي بوليمر١ وبوليمر١١ وبوليمر١١١ على التوالي بطريقة البلمرة التكثيفية بين الكليسيرول و التراي ايثانول امين مع الماليك انهيدرايد.

جميع البوليمرات تم تشخيصها بواسط FTIR و X-Ray حيث اظهرت البوليمرات كريستالية وفق الترتيب التالي

Polymer II> Polymer III>Polymer I

تم تشويب البوليمرات الثلاثة مع$LiClO_4$,$CuCl_2$, $NiCl_2$, $FeCl_2$

تم قياس التوصيلية المستمرة بمدى حراري يتراوح بين (٢٩٨-٣٧٣ كلفن) وان النتائج العملية أظهرت ان التوصيلية الكهربائية تزداد عدة مراتب عشرية مع زيادة درجة الحرارة، كفاءة المشوبات تزداد مع كفائتها الالكترونية كما معروف من خلال جهد الاختزال القياسي .

نتائج التوصيلية اظهرت ان البوليمر١١ يمتلك توصيلية اعلى من البوليمر١ ومن ثم بوليمر١١١ هذا في الحالة المشوبة اما في الحالة النقية فان البوليمر ١١١ يكون اعلى توصيلية من البوليمر١١ ومن ثم البوليمر١

تم حساب طاقة التنشيط للبوليمرات في الحالة المشوبة والنقية حيث اظهرت النتائج ان طاقة التنشيط تقل بازدياد االتوصيلية الكهربائية.

كما تم استخدام قياس التيار المتناوب لغرض حساب ثابت العزل الكهربائي للبوليمرات في الحالتين النقية والمشوبة.

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Summary

With in the frame of this work , cross-linked polymer prepared in different percents (25:75),(50:50%) and (0:100%) (glycerol:triethanol amine) which produced polymer I, polymerII and polymerIII consequently via condensation polymerization between glycerol and triethanol amine with malice anhydride.

All the polymers were identified by F.T.IR and X-Ray and the result showed that the crystillanity of the polymers as follow
Polymer II> polymerIII> polymer I

All the polymers were doped with CuCl2, $NiCl_2$, $FeCl_2$ and $LiClO_4$.

D.C. conductivity were measured in temperature range from (298-373 K) and the experimental result showed that the electrical conductivity increase several order magnitude with increasing temperature , the efficiency of dopant increase with its electronic efficiency as evaluated from the standard reduction potential .

The electrical conductivity result showed that polymer II posses the highest conductivity ,followed by polymerI and then polymer III this in the doped state while in the pure state polymerIII possess the highest conductivity , followed by polymer II and then polymer I .

The energy of activation is calculated from the variation of the conductivity of the three polymers with temperature using the Arrhenius equation.

The A.C. measurement is used to calculate the dielectric constant for the polymers in both pure and doped state

الإهداء

إلى نور الهدى... ومقلة العيون

الحبيب المصطفى

إلى من بذلا النفس لأجل أن أكون

والدتي و والدي

إلى القلوب التي ماتزال تنبض بالحب

أخواني و اخواتي

إلى كل من دعا لي دعوة خالصة

اصدقائي الاعزاء

إلى كل قلب خفق حباً وخوفاً علي

أهدي ثمرة جهدي

مصطفى

بسم الله الرحمن الرحيم

و علم آدم الأسماء كلها ثم عرضهم
على الملائكة فقال أنبئوني بأسماء
هؤلاء إن كنتم صادقين* قالوا
سبحانك لا علم لنا إلا ما علمتنا
انك أنت العليم الحكيم

صدق الله العظيم

سورة البقرة (الأيات٣٠,٣١)

Supervisor certification

I certify that this thesis was prepared under my supervision at the Department of Chemistry, College of Science, Al-Nahrain University as a partial requirements for the **Degree of Master of Science in Chemistry.**

Signature:
Name: Assist.Prof.Dr. Emaad Taha Bakir
Date:

In view of the available recommendation, I forward this thesis for debate by the Examining Committee.

Signature:
Name:
Head of Chemistry Department
College of Science
Al-Nahrain University

sExamining Committee's Certification

We, the Examining Committee, certify that we read this thesis and have examined the student *Mustafa Sabeeh Abdallh in* its contents and that, in our opinion; it is adequate as a thesis for the Degree of Master of Science, in Chemistry.

Chairman

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Date:

Supervisor / Member

Signature:
Name:
Date:

Approved for the College of Graduate Studies

Signature:

Name**: Assist. Prof. Dr. LAITH ABDUL AZIZ AL-ANI**

Address: Dean of the college of Science Al-Nahrain University

Date:

Chapter One

Introduction

Chapter one: Introduction

1.1. Introduction

Polymers such as common plastic are insulators [1]. The term "electrical conduction" is usually assigned to metals or alloys. The discovery of conducting polymers has opened a new branch in material research [2]. The idea that plastics could be made to conduct electricity would have been considered to be absurd. Indeed, plastics have been extensively used by the electronics industry because of this very property. They were utilized as inactive packaging and insulating material figure (1.1) gives the electrical conductivities of some common polymers.

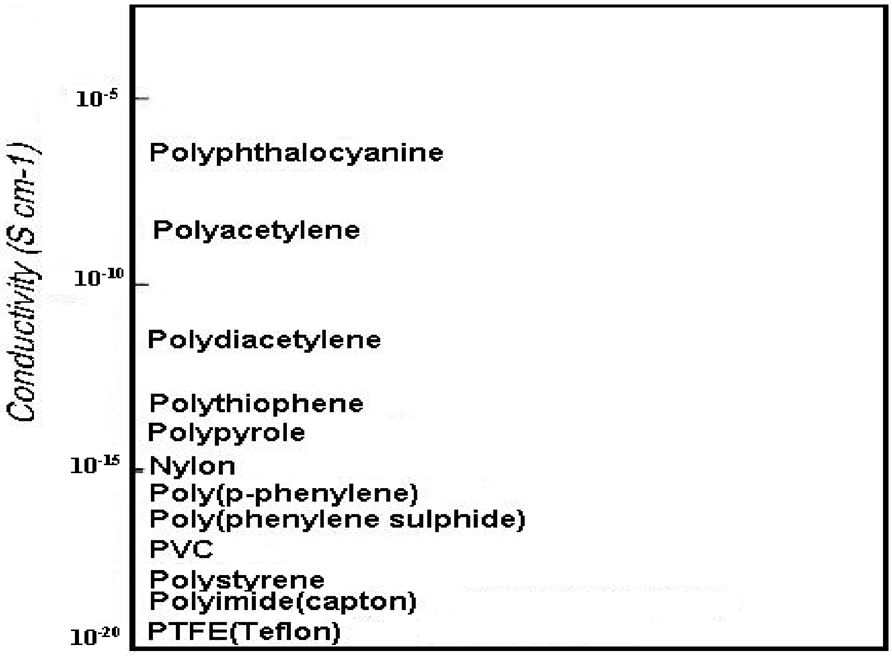


Figure (1.1) the electrical conductivities of some common polymers.

This very narrow perspective is rapidly changing as a new class of polymers known as intrinsically conductive polymers or electro active polymers are being discovered [3].

In 1910 Green and Woodhead reported that the electrical conductivity of polyaniline (Pani) was improved when the polymer was treated in acetic acid. However, this new discovery was forgotten. In the succeeding decades, chemists and physicists repeatedly tried to synthesize polymers with metallic conductivity. In the late 1950s and early l960s, Nattaetal and Luttiger synthesized polyacetylene but the product did not exhibit any conductive properties. Dall’Olio et al. prepared polypyrrole from aqueous sulphuric acid in 1969, but the product had poor in mechanical and electrical properties [4,5].

At the Plastics Research Laboratory of BASF in Ludwigshafen, Germany , the research priorities were centered on postulating new structural properties of polymers made by oxidative coupling. Copper chloride and aluminum chloride were used to make an oligobenzene from benzene. This reaction was extended to include other aromatic compounds and heterocycles. These reaction products were characterized in terms of thermoelectric power and photo and dark conductivities. To the researchers′ surprise, polyphenylene and polythiophene showed electrical conductivities of up to 0.1 S cm^{-1}. Not only was the highest value yet obtained, but also it was the first capable of conducting electricity [6]. These early attempts to synthesize organic materials with metallic-like conductivity aside, the works of MacDiarmid and Heeger and their coworkers [7,8] is considered the birthday of the electrically conducting polymers. These researchers have shown that poly conjugated polymers like polyacetylene undergo dramatic increase in their conductivities upon treatment with oxidizing or reducing agents as Iodine, SbF_5, Na and their like. They gave the term “dopants” to these reagents and the name “doping” to the process of adding these reagents to the polymers. Table (1.1) gives the conductivities of some doped poly conjugated polymers with the dopants reagents.

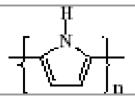
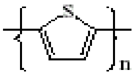
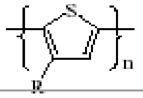
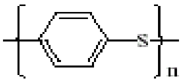
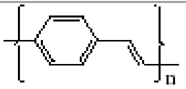
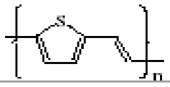
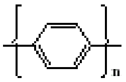
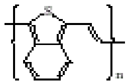
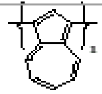
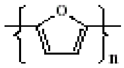
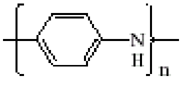
Polymer	Structure	Doping materials	$\Omega^{-1}cm^{-1}$ (Conductivity
Polyacetylene	$(CH)_n$	I_2, Br_2, Li, Na, AsF_5	10000
Polypyrrole		BF_4^-, ClO_4^-	500-7500
Polythiophene		BF_4^-, ClO_4^-	1000
Poly(3-alkylthiophene)		BF_4^-, ClO_4^-	1000-10000
Polyphenylene sulfide		AsF_5	500
Polyphenylenevinylene		AsF_5	10000
Polythienylenevinylene		AsF_5	2700
Polyphenylene		AsF_5, Li, Na	1000
Polyisothianaphthene		BF_4^-, ClO_4^-	50
Polyazulene		BF_4^-, ClO_4^-	1
Polyfuran		BF_4^-, ClO_4^-	100
Polyaniline		HCl	200

Table (1.1) common organic conducting polymers with their electrical conductivity in the doped state [8].

Since then, it has been found that about a dozen of different polymers and polymer derivatives undergo this transition when doped with an oxidation or reducing agent. They are all various conjugated polymers. This early work has led to the understanding of the mechanisms of charge storage and charge transfer in these systems. All have a highly conjugated electronic state. This also causes the main problems of the use of these systems, especially in terms of processibility and stability. Most early conjugated polymers were unstable in air and were not capable of being processed. The most recent research in this respect has been the development of highly conducting polymers with good stability and acceptable processing attributes [9, 10].

1.1.2. Electrical Conductivity

Conductivity is defined by Ohm's law:

$$U = R\,I \qquad (1.1)$$

Where I is the current (in Amperes) through a resistor and U is the drop in potential (in Volts) across it, the proportionality constant R is called the "resistance", measured in Ohms (Ω). R is measured by applying a known voltage across the resistor and measuring the current through it. The reciprocal of resistance (R^{-1}) is called *conductance*. Ohm's law is an empirical law, related to irreversible thermodynamics, the flow of I as a result of a gradient in potential leads to energy being dissipated (RI^2 Joule s^{-1}).

Not all materials obey Ohm's law. For instance, gas discharges, vacuum tubes, semiconductors and what are termed one-dimensional conductors (*e.g.* linear polyene chain) all deviate from Ohm's law. In Ohmic materials the resistance is proportional to the length l of the sample and is inversely proportional to the sample cross-section A:

$$R = \rho\, l / A \qquad (1.2)$$

Where ρ is the resistivity measured in Ω cm (in SI units. m) . Its inverse (ρ^{-1}) is the *conductivity*(σ). The unit of conductance is the Siemens ($S = \Omega^{-1}$). The unit of conductivity is S m^{-1}.

Conductivity depends on the number density of charge carriers (number of charge carriers n) and how fast they can move in the material (mobility μ):

$$\sigma = n\mu e \qquad (1.3)$$

Where (e) is the electron charge. In semiconductors and electrolyte solutions, one must also add in eq (1.3) an extra term due to the positive charge carriers (holes or cations).

Conductivity depends on temperature: it generally increases with decreasing temperature for “metallic” materials (some of which become superconductive below a certain critical temperature (Tc), while it generally decreases with lowered temperature for semiconductors and insulators [11, 12]. Figure (1.2) shows the effect of temperature on the conductivity for metals and semiconductors and insulators.

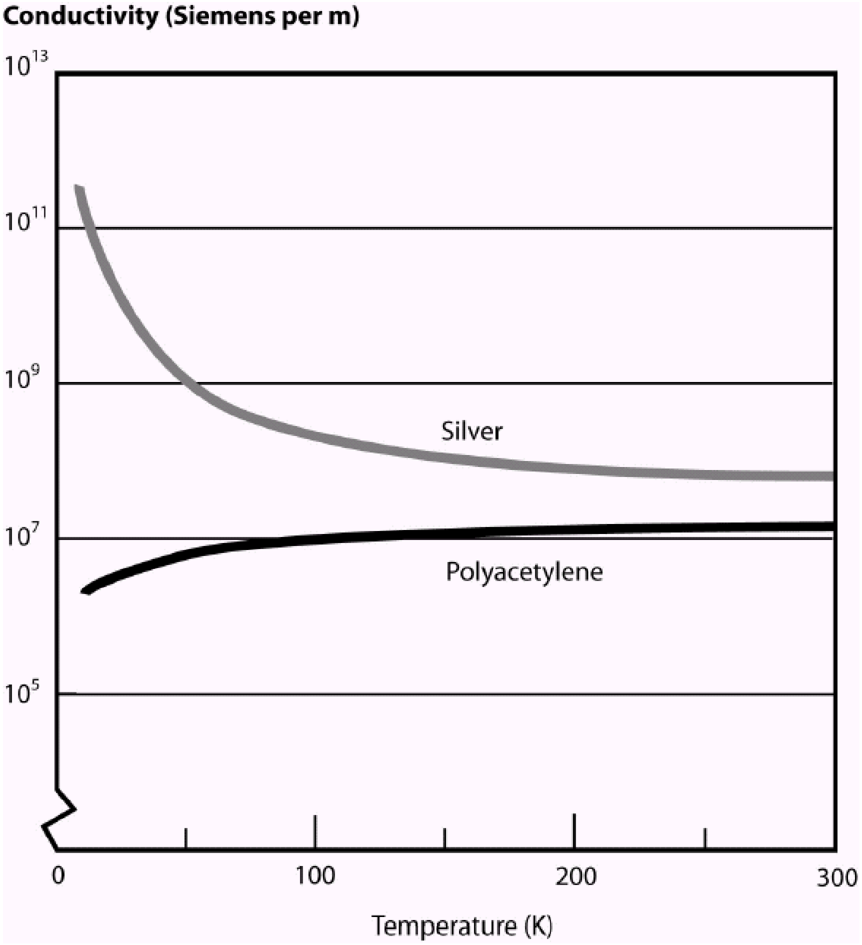


Figure (1.2) the conductivity of conductive polymers decreases with falling temperature in contrast to the conductivities of typical metals, e.g. silver, which increase with falling temperature[11].

1.1.3. What Makes a Material Conductive?

In many materials, such as crystals, stretched polymers or liquid crystals, macroscopic properties such as strength and optical and electrical properties generally depend on direction. They are said to be *anisotropic*. Similarly, the material's electrical conductivity may depend on direction and be anisotropic. Three simple carbon compounds are diamond, graphite and polyacetylene. They may be regarded, respectively, as three-two- and one-dimensional forms of carbon materials (Fig 1.3). Diamond and graphite are modifications of pure carbon, while in polyacetylene one hydrogen atom is bound to each carbon atom.

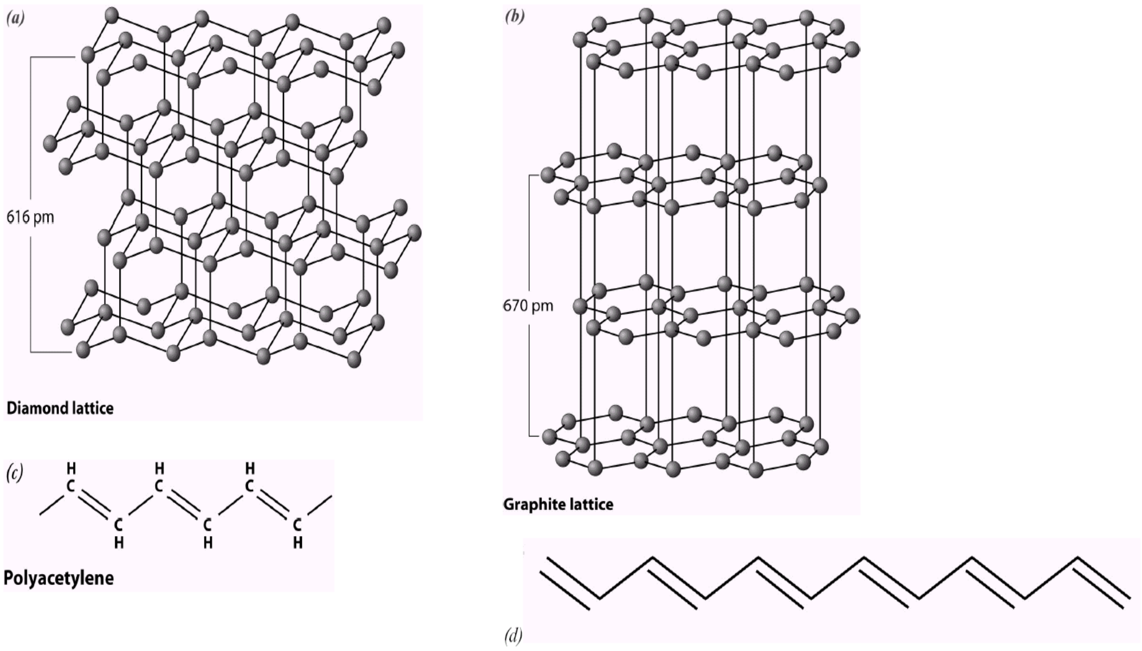


Figure (1.3) Three-, two- and one-dimensional carbon materials: diamond (a) and graphite (b) crystal lattices, and polyacetylene chain (c). An alternative way of writing polyacetylene is also shown (d).

Diamond, which contains only σ bonds, is an insulator and its high symmetry gives it isotropic properties. Both graphite and acetylene have mobile π electrons and are, when doped, highly anisotropic metallic conductors. Conductivity is about one million times greater in the plane of the graphite rings than at right angles to this plane: σ (parallel)/ σ(perpendicular) = 10^6 . Correspondingly, the conductivity of stretch-oriented polyacetylene is some 100 times higher in the stretch direction than perpendicular to it.

The smaller anisotropy compared to graphite, *i.e.* non-vanishing σ (Perpendicular) could suggest”short-circuiting” across the chains. Since the polyacetylene chains are not infinite, contacts between them are important if the material is to be macroscopically conductive. This could thus explain the lower conduction anisotropy compared to graphite [13].

1.2 Metal-Containing Conducting polymers

Metal containing conducting polymers are a new and interesting class of materials that combine some of the redox properties of the conducting polymer and some of those of the metal ions [14-16].

Metal containing conducting polymers materials can be divided into three major types. Type I material consist of metal center tethered to the conjugated polymer backbone through a saturated linker such as alkyl group. In this case, the polymer backbone mainly acts as a conductive support, and the properties of the metal center are essentially unchanged. In type II materials, the metal center and the conjugated polymer backbone are electronically coupled, often by use a conjugated linker or by coordination to sites directly on the backbone, and can influence each other's properties. In type III materials the metal centers are located directly within the conjugated backbone. In this configuration, strong interaction between the metal center and the organic bridge is possible. Figure (1.4) gives the schematic representation of the three types of metal containing conducting polymers [17].

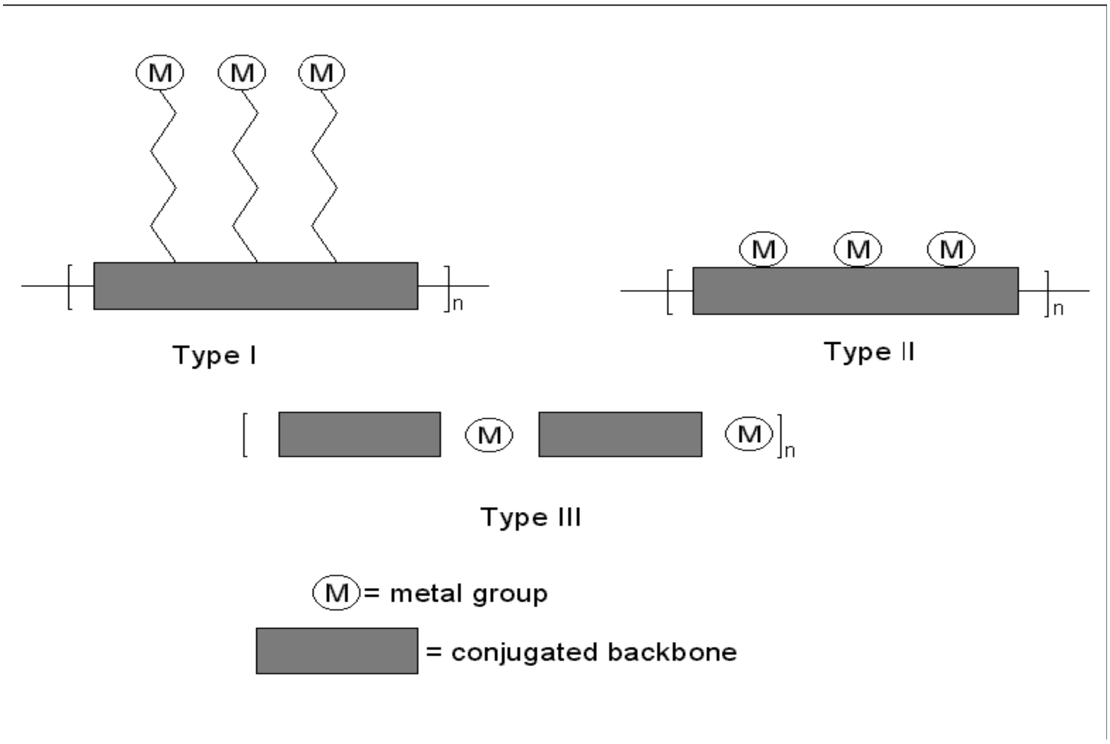


Figure (1.4) Schematic representations of the three types of metallopolymers [14].

1.3. Doping mechanism

In a metal, there is a high density of electronic states with electrons with relatively low binding energy, and the ”free electrons” move easily from atom to atom under an applied electric field. The conductivity of the material can be measured by standard procedures; a value for metallic copper around 10^8 S m^{-1} has been measured. The electrical properties of a material are determined by its electronic structure [18]

Most organic materials, however, do not have intrinsic charge carriers.

The required charge carriers may be provided by partial oxidation

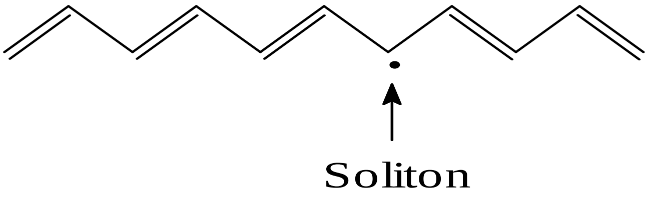
(p-doping) of the organic (macro) molecules with electron-acceptors

(e.g. I2, AsF5) or by partial reduction (n-doping) with electron-donors (e.g. Na, K). Through such a doping process, charged defects are introduced, which could then be available as the charge carriers [19-21].

$$[\mathrm{CH}]\,n + 3x/2\ \mathrm{I_2} \longrightarrow [\mathrm{CH}]\,n^{x+} + x\mathrm{I_3}^{-} \quad \textbf{oxidative doping}$$
$$[\mathrm{CH}]\,n + x\mathrm{Na} \longrightarrow [\mathrm{CH}]\,n^{x-} + x\mathrm{Na}^{+} \quad \textbf{reductive doping}$$

The main criterion is its ability to oxidize or reduce the polymer without lowering its stability [22] or whether or not they are capable of initiating side reactions that inhibit the polymers ability to conduct electricity. An example of the latter is the doping of a conjugated polymer with bromine. Which is a powerful an oxidant and adds across the double bonds to form sp^3 carbons. The same problem may also occur with $NaPF_6$ if left too long [23, 24].

One of the attempts to explain the high conductivity of acetylene by Su and his coworkers in term of soliton[25,26]. Soliton is a structural defect in the form of non-bonding electron formed in trans-polyacetylen when two conjugated in the opposite direction are in the same chain.



Soliton can be formed by adding or drawing an electron in the doping process, it has the ability to move along the chain so it can be considered as charge carrier.

This defect leads to formation of new energy level in polymeric chain which can be occupied by one electron to be neutral or by two to be negative or empty and it will be positive. Figures (1.5) illustrate the types of soliton.

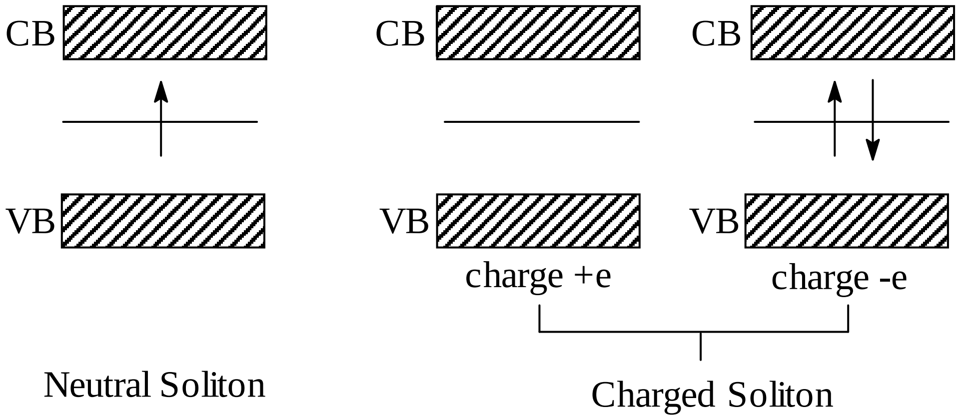


Figure (1.5) energy levels for the three types of soliton [26].

There is another type of charge carriers. However, when two neutral solitons are combine they will form a double bond, and if charge soliton combine with neutral one causing a level of lower energy called "Polaron" [27].while in the case of combining of two charged solitons ,they form "bipolaron"[28] .

1.3.1. Hopping Mechanism

Bulk conductivity in the polymer material is limited by the need for the electrons to jump from one chain to the next, *i.e.*, in molecular terms, an intermolecular charge transfer reaction. It is also limited by macroscopic factors such as bad contacts between different crystalline domains in the material, the charge carrier are impeded by "phase boundaries"[29].

One mechanism proposed to account for conductivity by charge-hopping between different polymer chains is”intersoliton hopping”

(Figure 1.6). Here an electron is jumping between localized states on adjacent polymer chains; the role of the soliton is to move around and to exchange an electron with a closely located charged soliton, which is localized. The mechanism at work in intersoliton hopping is very similar to that operating in most conducting polymers somewhere between the metallic state at high doping and the semiconducting state at very low doping. All conjugated polymers do not carry solitons, but polarons can be found in most of them. Charge transport in Polaron-doped polymers occurs via electron transfer between localized states being formed by charge injection on the chain [30-32].

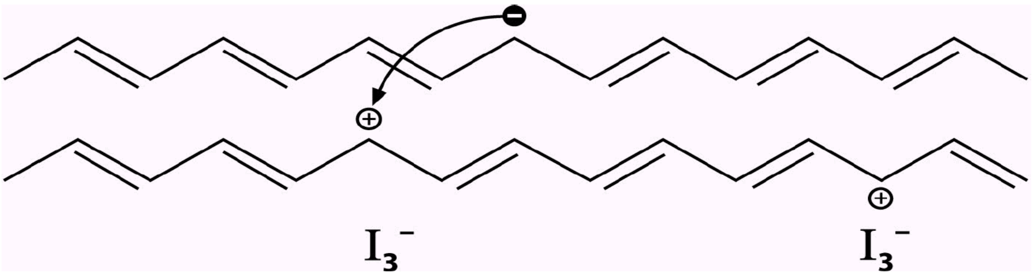


Figure (1.6). intersoliton hopping: charged solitons (bottom) are trapped by dopant counterions, while neutral solitons (top) are free to move. A neutral soliton on a chain close to one with a charged soliton can interact: the electron hops from one defect to the other[32].

The theoretical calculation[33,34] and practical result[35] showed that the conductivity in this disordered system depends on temperature and frequency of the current used which improved that hopping mechanism controlling on this system which not increasing the concentration of charge carrier but the mobility of the carrier and increase the probability of hopping process.

1.3.2. Doping methods

1-Gas-phase doping

This process include passing of gas represent the dopant material or gas containing the doping material through container containing polymer, this process can be use for dopant which can be easily found in gas phase like Bromine and Iodine.[36]

2-Solution doping

This process done by use vaporizes inert solvent to dissolve the dopant material and the polymer immersed for a period of time to allow the dopant molecules to diffuse in the polymer chains [36-38].

3-Doping by mixing

This process done by direct mixing of polymer with dopants , in this case the two material grind and mixed for along period of time to ensure homogenous contributing of dopant between the polymer chains .[37,39]

4- Electrochemical method

This method used in doping of polymers prepared by chemical polymerization method, as we mentioned before, doping of conjugate polymer is a redox process so it is possible to do this process electrochemically by oxidation on anode or reduction on cathode in which the polymer precipitate as a thin layer on electrodes using a solvent having high dielectric constant like acetonitrile and high dissociation constant called "supporting electrolyte" like tetra ethyl ammonium perchlorate, In the case of oxidation on anode ,the generated positive charges neutralize by negative ion derived from the supporting electrolyte which operate as a counter ion[37,40,41]. .

1.4 Stability

There are two distinct types of stability. Extrinsic stability is related to vulnerability to external environmental agent such as oxygen, water, and peroxides. This is determined by the polymer susceptibility of charged sites to be attacked by nucleophiles, electrophiles and free radicals.

If a conducting polymer is Extrinsic and unstable, then it must be protected by a stable coating. Many conducting polymers, however, degrade over time even in dry, oxygen free environment. This intrinsic instability is thermodynamic in origin. It is likely to be caused by irreversible chemical reaction between charged sites of polymer and either the dopant counter ion or the π-system of an adjacent neutral chain, which produces an sp^3 carbon, thus breaking the conjugation. Intrinsic instability can also come from a thermally driven mechanism, which causes the polymer to lose its dopant. This happens when the charge sites become unstable due to conformational changes in the polymer backbone. This has been observed in alkyl substituted polythiophenes[42-44].

1.5 Processibility

Conjugated polymers may be made by a variety of techniques, including cationic, anionic, radical chain growth, co-ordination polymerization, step growth polymerization or electrochemical polymerization. Electrochemical polymerization occurs by suitable monomers, which are electrochemical oxidized to create an active monomeric and dimeric species, which react to form a conjugated polymer backbone [45]. The main problem with electrically conductive Plastics stems from the very property that gives it its conductivity, namely the conjugated backbone [46]. This causes many polymers to be intractable, insoluble films or powders that cannot melt. There are two main strategies to overcome these problems. Namely the modification of the polymer so that it may be more easily processed, or manufacturing it in its desired shape and form [47, 48].

One of the attempts to overcome this problem is the synthesis of copolymers or derivatives of a parent conjugated polymer with more desirable properties. This method is the more traditional one for making improvements in a polymer. What is done is to try to modify the structure of the polymer to increase its processibility without compromising its conductivity or its optical properties. All attempts to do this on polyacetylene have failed as they always significantly reduced its conductivity[14]. However, attempts on polythiophenes[49] and polypyrroles have been proved more fruitful. The hydrogen on carbon 3 on the thiophene or the pyrrole ring was replaced with an alkyl group with at least four carbon atoms in it. The resulting polymer, when doped, has a comparable conductivity to its parent polymer whilst is able to melt and it soluble. Placing carboxylic acid group or sulphonic acid group on the alkyl chains has produced a water-soluble version of these polymers. If sulphonic acid groups are used along with built-in ionizable groups, such a system can maintain charge neutrality in its oxidized state and so they effectively dope themselves. Such polymers are referred to as "self-doped" polymers. One of the most highly conductive derivative of polythiophene is made by replacing the hydrogen on carbon three with a -CH_2-O-CH_2CH_2-O-CH_2CH_2-O-CH_3. This is soluble and reaches a conductivity of about 1000 S cm^{-1} upon doping.[50,51].Table (1.2) shows the stability and processibility of some conducting polymers.

Table (1.2) stability and processing attribute of some conducting polymers

Polymer	Conductivity S cm^{-1}	Stability (doped state)	Processing Possibilities
Polyacetylene	10^3 - 10^5	Poor	Limited
Polyphenylene	1000	Poor	Limited
PPS	100	Poor	Excellent
PPV	1000	Poor	Limited
Polypyrroles	100	Good	Good
Polythiophenes	100	Good	Excellent
Polyaniline	10	Good	Good

1.6 Nonconjugated Conductive Polymers

As we mentioned before, that polymers could conduct electricity if they have conjugated system, but this is not a rule, conjugation is not a prerequisite for a polymer to be conductive[52] A polymer must have at least one double bond in the repeating unit to become conductive. Interaction with a dopant (e.g. electron acceptor) causes transfer of an electron from the double bond to the dopant creating a hole at the double bond site. Electrical conduction occurs via intersite hopping of holes. Various spectroscopic methods (FTIR, optical absorption, solid-state ^{13}C NMR etc.) have been used to characterize nonconjugated conductive polymers. Examples of these polymers include 1,4-polyisoprene, which has one double bond and three single bonds in the repeating unit[53,54] The conductivity of polyisoprene increases 100 billion times upon doping with iodine to a maximum value of 10 Sm^{-1}. Polyisoprene (natural rubber) is used in large volumes for various commercial applications. Doped polyisoprene and other nonconjugated conductive polymers have a wide range of applications in antistatics, various sensors and optoelectronics [55].

1.7 Applications

The extended π-systems of conjugated polymers are highly susceptible to chemical or electrochemical oxidation or reduction. These alter the electrical and optical properties of the polymer. By controlling oxidation and reduction, it becomes possible to precisely control such properties. Since these reactions are often reversible, it is possible to control the electrical and optical properties systematically and with great deal of precision. It is even possible to switch from a conducting state to an insulating one.

There are two main groups of applications for these polymers. The first group utilizes their conductivity as its main property. The second group utilizes electroactivity.

They are shown below:

Group 1	**Group 2**
Electrostatic materials	Molecular electronics
Conducting adhesives	Electrical displays
Electromagnetic shielding	Chemical and biochemical sensors
Printed circuit boards	Rechargeable batteries
Artificial nerves	Drug released systems
Antistatic clothing	Optical computers
Thermal sensors	Ion exchange membranes
Piezoceramics	Electromechanical actuators
Active electronics	'Smart' structures
Switches	
Aircraft structures	

The principal interest in the use of polymers lies in its low-cost manufacturing by using solution-processing of film-forming polymers. Light displays and integrated circuits, for example, could theoretically be manufactured using simple inkjet printer techniques. Below are the main applications of some conducting polymers:

Doped Polyaniline is used as a conductor and for electromagnetic shielding of electronic circuits. Polyaniline is also manufactured as a corrosion inhibitor.

Poly (ethylenedioxythiophene) (PEDOT) doped with polystyrenesulfonic acid is manufactured as an antistatic coating material to prevent electrical discharge exposure on photographic emulsions and also serves as a hole injecting electrode material in polymer light-emitting devices.

Poly (phenylenevinylidene) derivatives have been major candidates for the active layer in pilot production of electroluminescent displays (mobile telephone displays).

Poly (dialkylfluorene) derivatives are used as the emissive layer in full-color video matrix displays.

Poly (thiophene) derivatives are promising for field-effect transistors They may possibly find a use in supermarket checkouts.

Poly(pyrrole) has been tested as microwave-absorbing "stealth" (radar-invisible) screen coatings and also as the active thin layer of various sensing devices.

Other possible applications of conductive polymers include supercapacitors and electrolytic-type capacitors. Some conductive polymers such as Polyaniline show a whole range of colors as a result of their many protonation and oxidation forms. Their electrochromic properties can be used to produce, *e.g.* "smart windows" that absorb sunlight in summer. An advantage over liquid crystals is that polymers can be fabricated in large sheets and unlimited visual angles. They do not generally respond as fast as in electron-gun displays, because the dopant needs time to migrate into or out from the polymer - but still fast enough for many applications [56-59].

1.8 Aim of the work

In the electronic industry, there is a need for materials of different electrical conductivities ranging from the semi-conducting to the conducting region. In addition the materials should be easily processable and stable .

The synthesis of new electrically conducting polymers with different chemical structures provides an efficient method for the introduction of new materials with the qualifications described above. Furthermore, knowledge of the electrical behavior of a great member of polymers with various chemical structures enables us to understand the relationship between the electrical behavior and chemical structure, which form the basis for the invention of new polymers with improved properties.

In this work, three polymers differ in each other in the percent of nitrogen atoms and in the structure, these polymers are doped with different metal salts ($CuCl_2$, $NiCl_2$,$FeCl_2$ and $LiClO_4$)and study the electrical properties of the polymers in both pure and doped state at temperature ranged from (25-100 $^{\circ}C$).

Chapter
Three

Results & Discussion

Conclusion

The following conclusions have been reached out:

1- The structure of the polymer has an important effect on the conductivity of the polymers in the pure and doped state.

2- The electrical conductivity of the polymers was enhanced with addition of metal salts.

3- The electrical conductivity of the polymers in both pure and doped state was enhanced with increasing temperature.

4- The activation energy is decreased with increasing the conductivity.

5- In A.C measurement, the dielectric constant (ἐ) is decreased with increasing the frequency.

Suggestion for future work

1- Using another group of transition metals and study of their electrical properties or other features of interest.

2- Study of the optical properties of the polymers in both pure and doped state.

3- The electrical properties of polymeric composites require investigation of various concentrations of the dopants.

4- Study of thermal and mechanical properties of the prepared polymers.

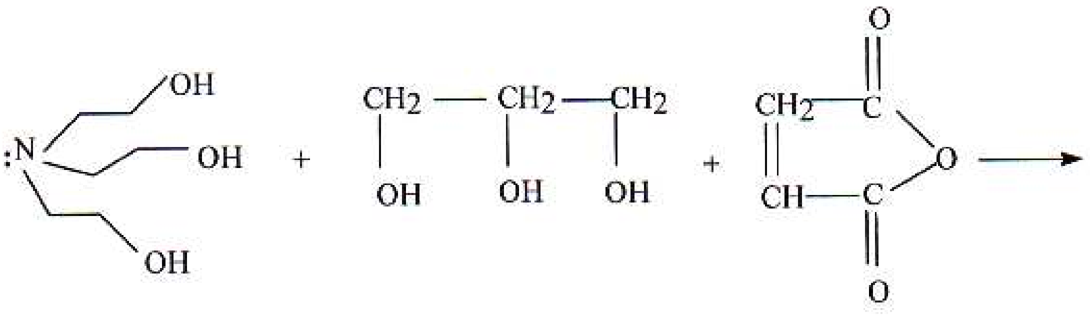
5- Study the effect of time on the conductivity of the polymers in the doped state.

Chapter three: Results and discussion

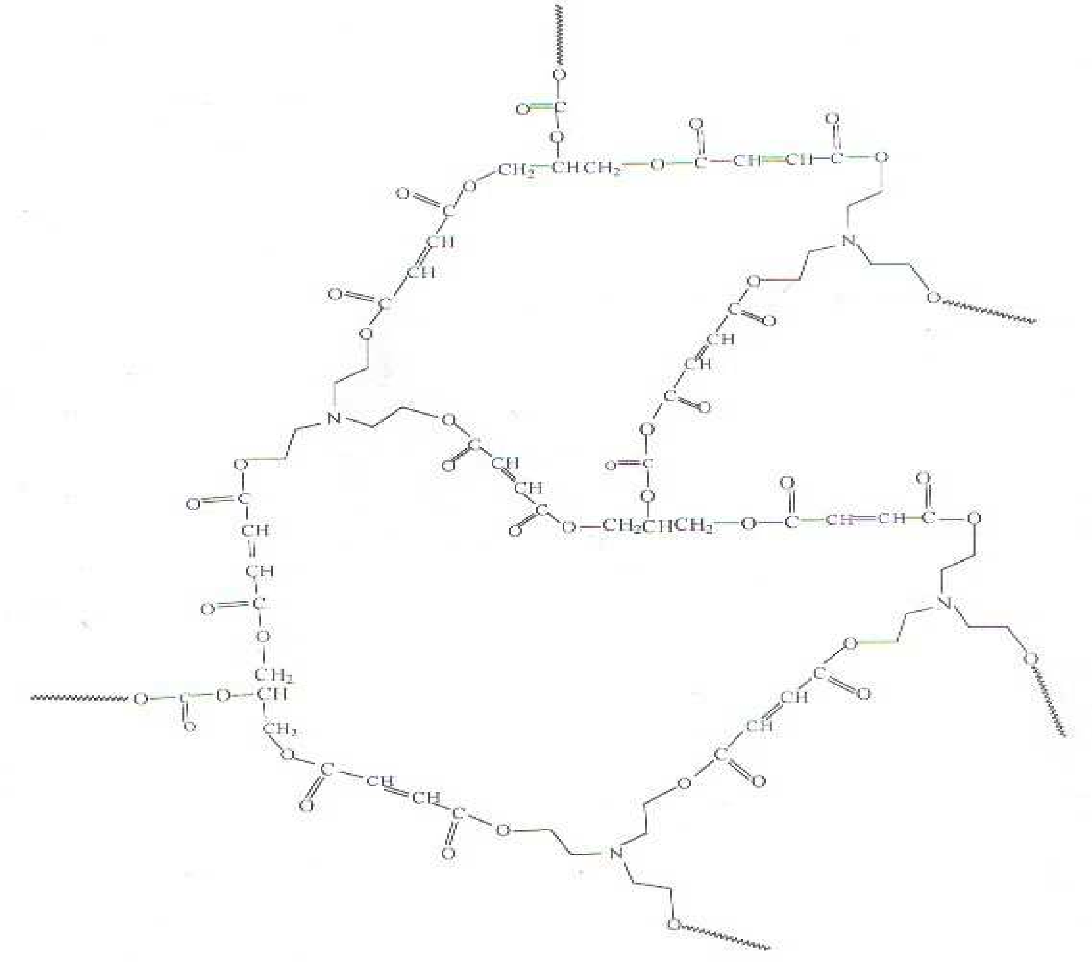
3.1 Polymer synthesis

It is known that condensation reaction of glycerol with maleic anhydride produce hard and rigid polymer [6٣]. On the other hand , we found that condensation of triethanolamine and glycerol with maleic anhydride produce less hard and rigid polymers (polymer I, II) while the condensation of triethanolamine with maleic anhydride produces polymer(polymer III) tend to be elastic.

As in the following chemical reaction scheme (3.1) for polymer (I and II), and scheme (3.2) for polymer (III).

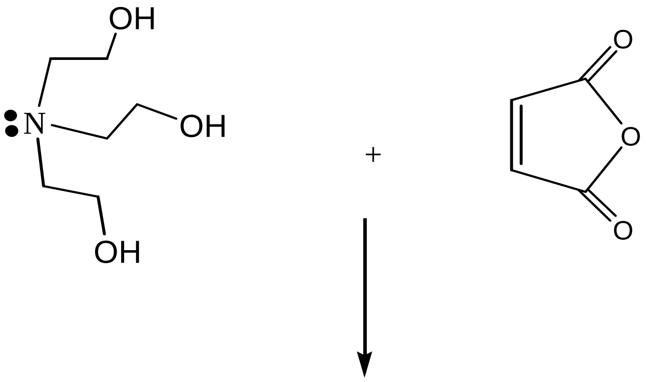


Triethanolamine Glycerol Maleicanhydrid

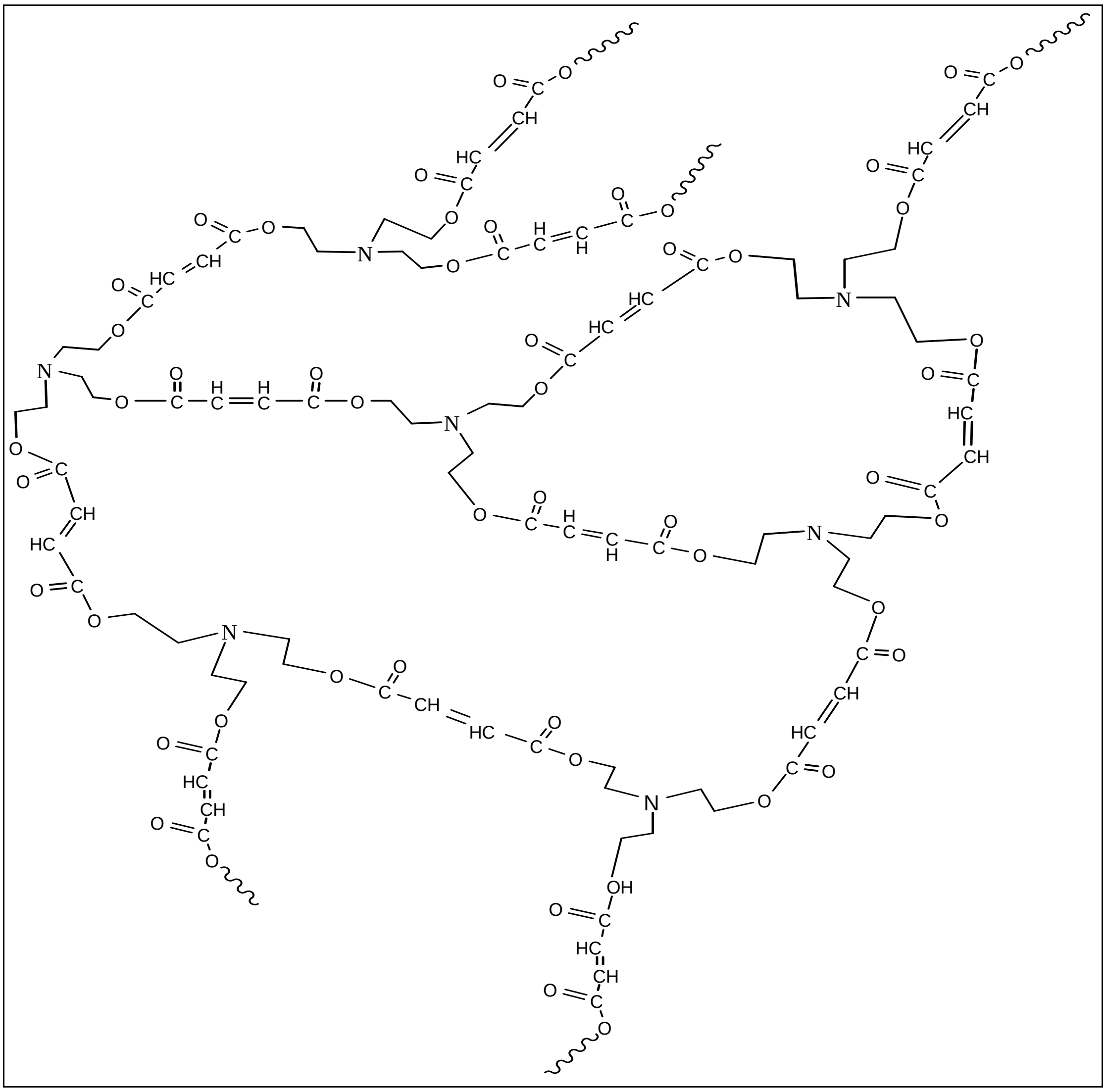


Scheme (3.1) the suggested structure of polymers I and II

Reaction of polymer III



Triethanolamine Maleicanhydrid



Scheme (3.2) the suggested structure of polymer III

Despite the synthesis of the polymers (I, II and III) are the same, but we believe that polymer III contains more Nitrogen atoms which may play significant role in the electrical conduction.

3.2 Polymer characterization

All the prepared polymer are characterized by the difficult solubility in most solvents, that because of the high degree of cross linking which prevent the rotation of the bonds and consequently the molecule have high energy barrier to solvation process and for this reason we can not determine the molecular weight and the degree of polymerization.

However, the polymers [I, II and III] were identified by FTIR spectrum. The FTIR spectrum of polymers [I] and [II] showed the appearance of the characteristic absorption bands at (1732 cm^{-1}) due to the stretching vibration of the (C=O) of the forming ester. A band at (1161 cm^{-1}) was due to the (C-O) stretching of ester and appearance of (C-N) band at (1296 cm^{-1}), a band of (C=C) appears at (1639cm^{-1})and also a band at (2943cm^{-1}) due to C-H aliphatic.

Also, the FTIR spectrum of polymer [III] showed the appearance of the band at (1732 cm^{-1}) due to v(C=O) of ester. A band at (1161 cm^{-1}) was due to the (C-O) stretching of ester and appearance of (C-N) band at (1288cm^{-1}), a band of (C=C) appears at (1639cm^{-1})and also a band at (2943cm^{-1}) due to C-H aliphatic. The FTIR spectra of the above polymers are shown in figs. (3.1) and (3.2).

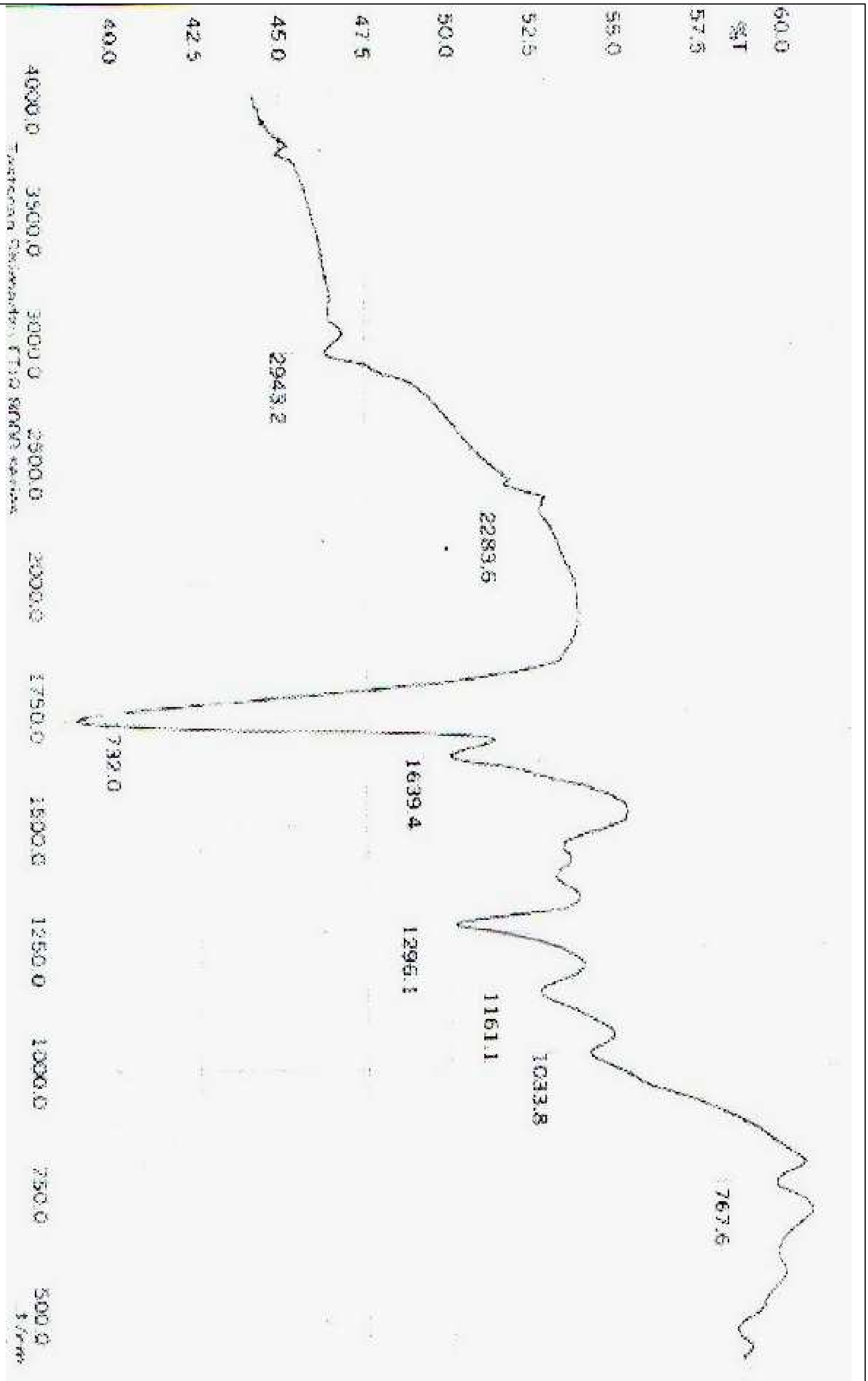


Figure (3-1): F.T.IR spectrum of polymers (I&II)

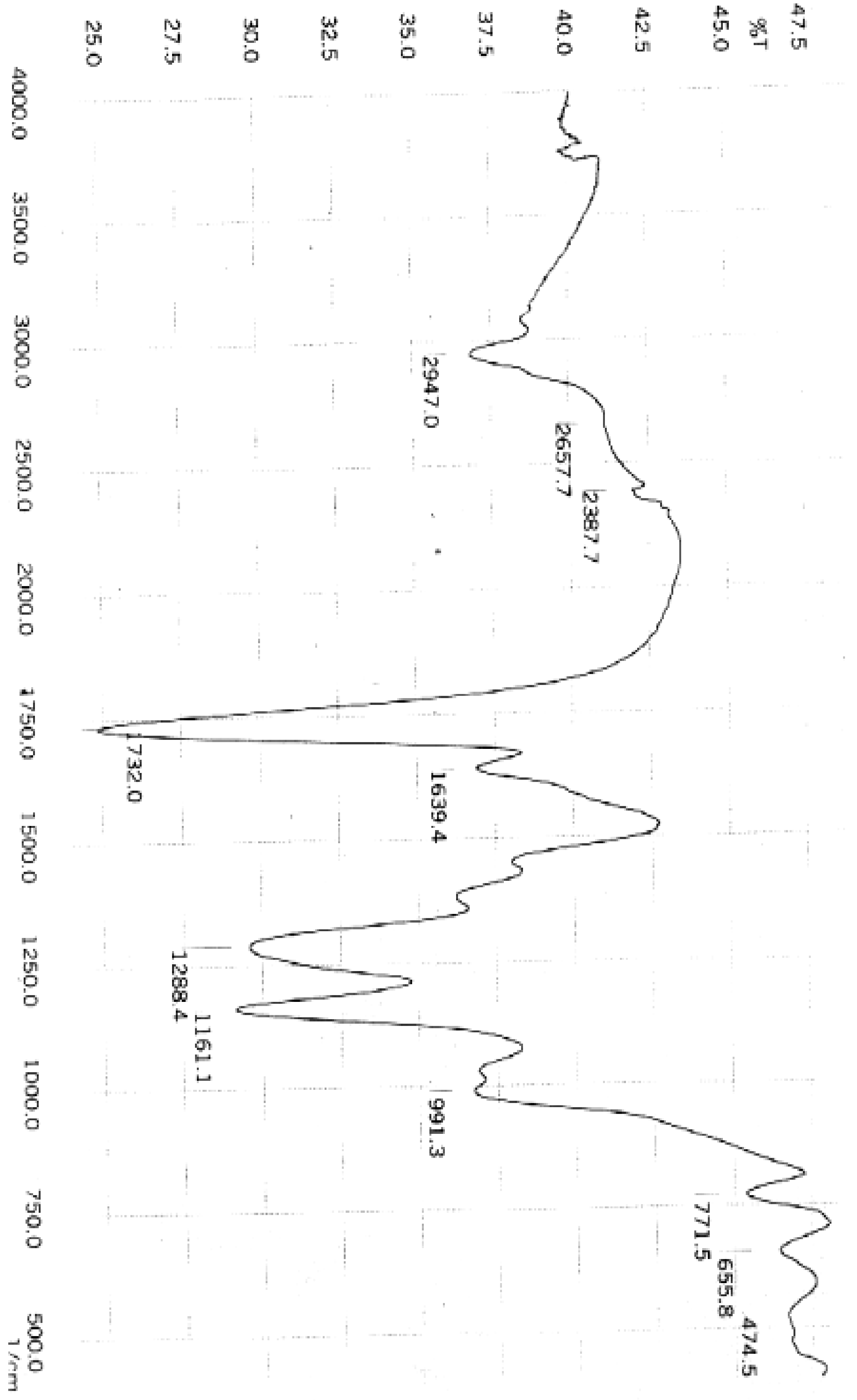


Figure (3-2): F.T.IR spectrum of polymer (III)

X-ray diffraction is also used to identify the nature of the polymers whether crystalline or not.The results showed that the polymers have different crystillanity form in which the polymer II revealed crystalline nature greater than polymer III as in the figures (3.4) and (3.5).

Polymer I exhibit amorphous nature as in the figure (3.3).

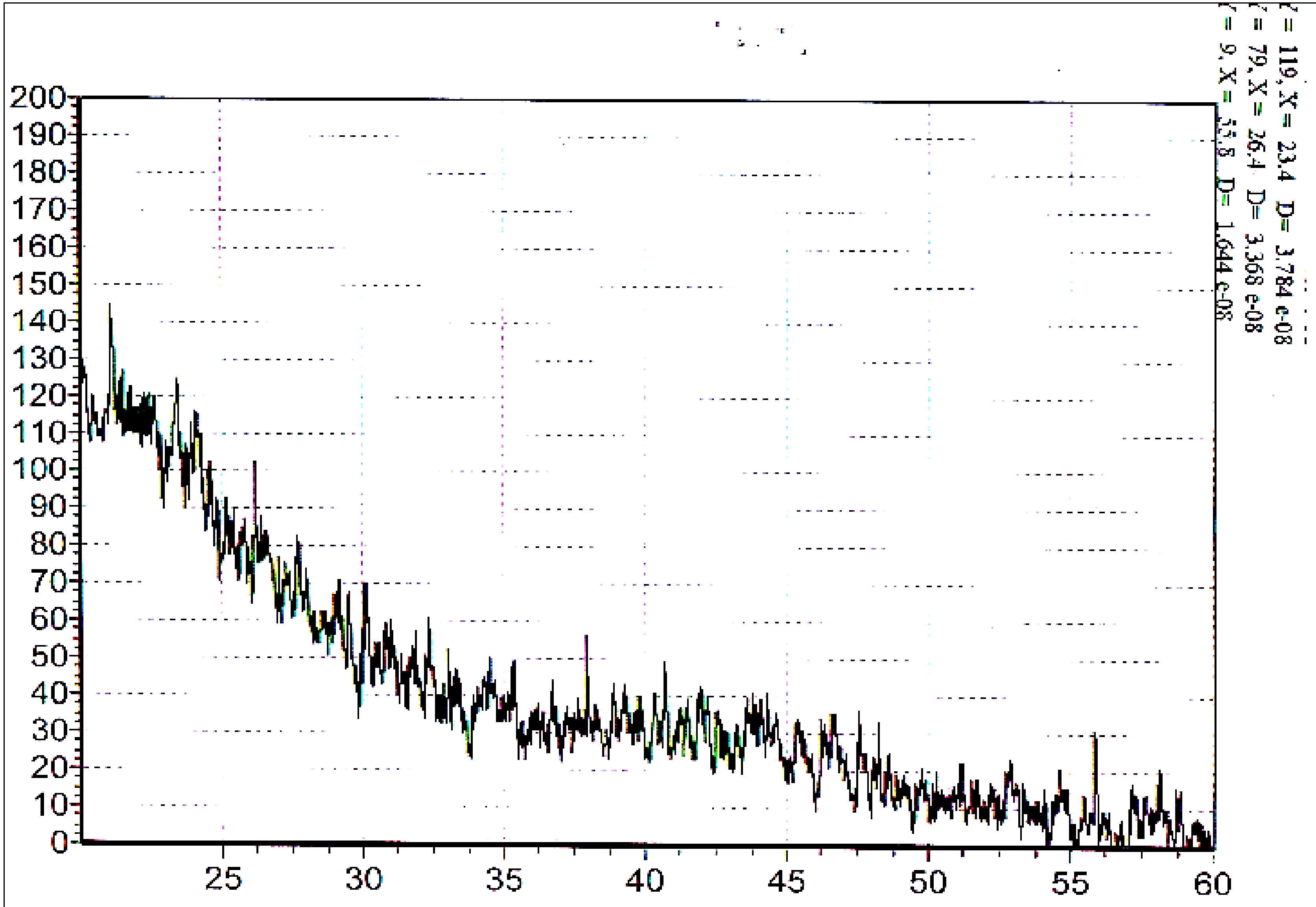


Figure (3-3): X-ray diffraction of polymer I

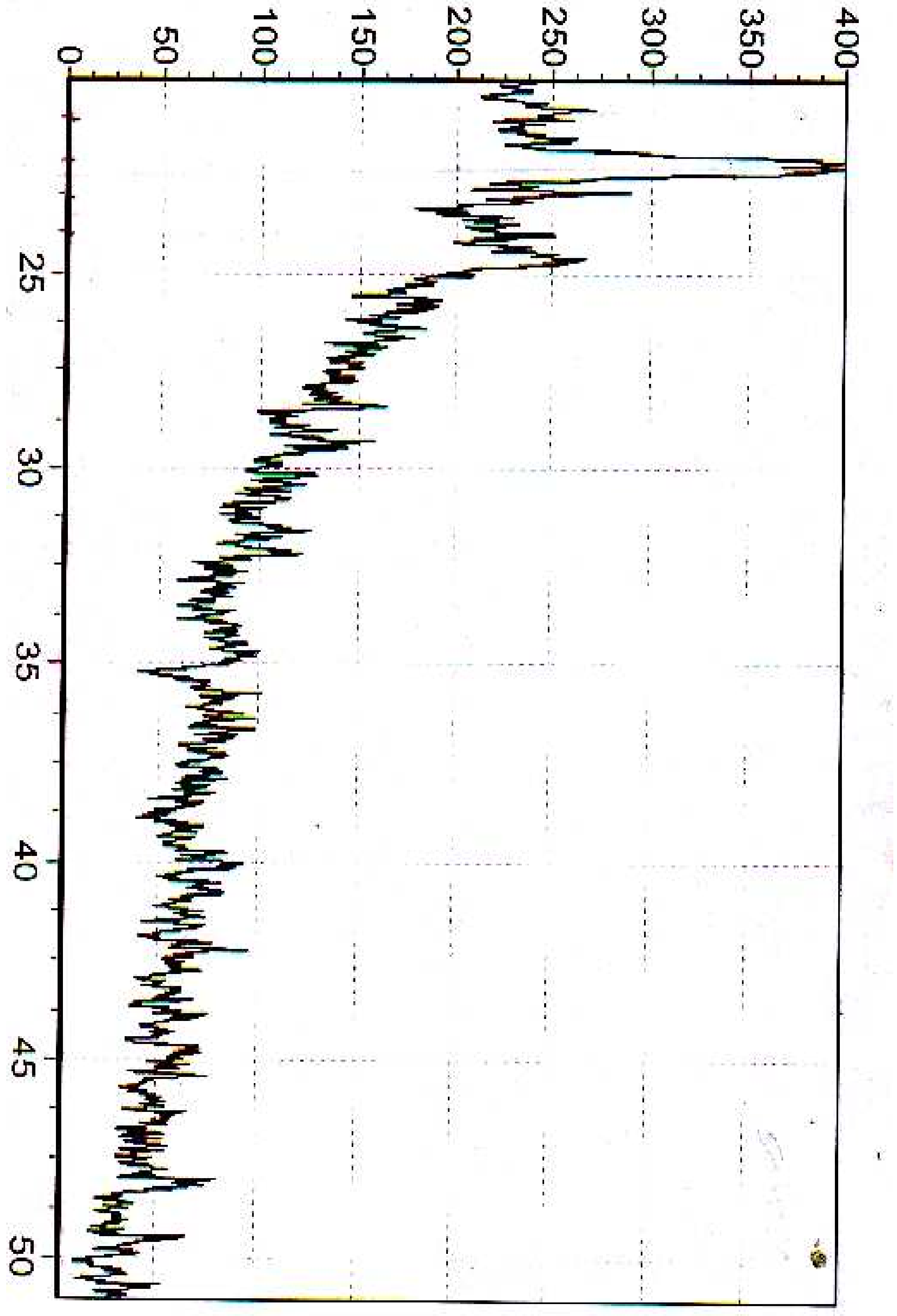


Figure (3-4): X-ray diffraction of polymer II

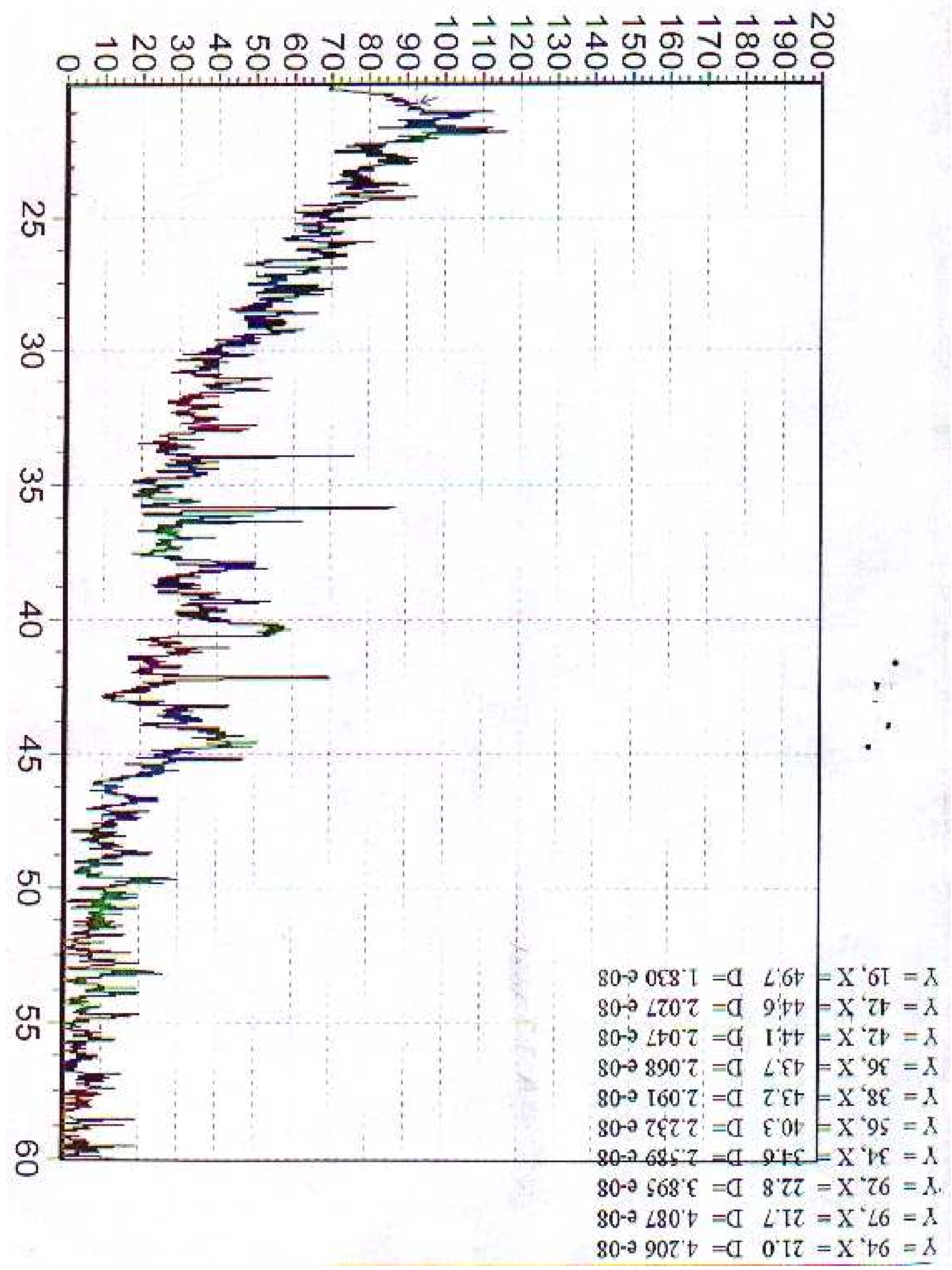


Figure (3-5): X-ray diffraction of polymer III

3.3 Electrical measurements

3.3.1 D.C Measurements

3.3.1.1 Nature of the interference between the polymer and the dopants

The different changes in the electrical conductivity property of the polymers after being doped by different ionic dopants leads to thought of the presence of a special interaction of type metal-polymer plays important role in making these changes. There are many attempts to give an explanation for the nature of this interaction.

Seiblles [6٤] cleared that the differences in IR spectra for polar polymers doped with ($CoCl_2$, $CuCl_2$, $FeCl_3$) dopants can be explained through complex formation between these dopants and the polar functional group in these polymers.

In another study on polyether-poly(N,N'-dimethylacrylamid)-$LiClO_4$ has showed that the interaction of lithium cations with polyether oxygen and the carbonyl oxygen of poly(N,N'-dimethylacrylamide) leads to formation of complex[6٥] , so we can conclude that doping process of the polymers with different metal salts, generally, leads to formation of a special type of complexes between the metal cation and the functional groups of these polymers and these complexes can effect on the charge transfer between the polymer and the dopants and consequently on electrical conduction of doped polymers.

These complexes can be formed between two molecules, one can donate electrons (Lewis base) and the other can accept these electrons (Lewis acid).

3.3.1.2 Effect of physical properties of dopants on the conductivity of doped polymers

As we mentioned before the conductivity of polymers increase considerably when treated with definite low-molecular weight compounds termed "Dopants" through the formation donor-acceptor complex between the dopant and the polymer.

Their efficiency depends on the ionization potential of the polymer and the electron affinity of the dopants. [6٦] And usually use standard reduction potential as a good way to measure the electron affinity [6٧]. However, table (3.1) showed highest conductivity value relation with standard reduction potential of the three polymers in doped stat.

Dopant	Standard reduction potential, $^{\circ}E$	Highest conductivity Scm^{-1}		
		Polymer I	Polymer II	Polymer III
Cu^{+2}	**0.15**	**6.470E-6**	**1.429E-5**	**3.042E-6**
Ni^{+2}	**-0.24**	**9.908E-6**	**9.735E-06**	**1.513E-6**
Fe^{+2}	**-0.44**	**3.810E-7**	**5.509E-6**	**4.987E-7**
Li^{+1}	**-3.04**	**1.499E-5**	**2.251E-5**	**3.812E-6**

Table (3.1) the relation between the highest conductivity value with standard reduction potential of polymers (I, II, and III) in doped stat.

The highest conductivity value was obtained from doping of the three polymers with different dopnts as a function of standard reduction potential of the dopant material; hence, there is a direct relation between the efficiency of the dopants in supporting the electrical conduction with standard reduction potential.

From table (3.1) we notice that the Li^+ had shown a deviation from this role, which may be due to the small size of Li^+ ion, so it can diffuse easily in the polymer in addition to the high conductivity of Li^+ ion due to the charge to size ratio. While the conductivity of $CuCl_2$ is less than expected value due to the high electron affinity of Cu^{+2} ion and that because of the electronic configuration of the outer shell of Cu^{+2} ion ($3d^{10}$ $4s^0$) after accepting electron from the polymer, and became in more stable state with low tendency to loss this electron and back to unstable state.

3.3.1.3 Effect of temperature on the conductivity of the polymers in the pure and doped stat

It is known that the conductivity of traditional semiconductors like Silicone and Germanium increased with increasing temperature and that because of the increasing the charge carriers in the conduction band , on the another hand, research have proved that the conductivity in polymers , generally, depends on the temperature in the same way to semiconductors. However, tables (3.2) to (3.16) and figures (3.6) to (3.20) indicate the relation between the temperature and their effect on conductivity of the polymers (I, II and III) in both pure and doped state, the achieved experiments showed that their was an obvious decrease in polymer resistance (i.e., increasing conductivities) with increasing temperature in a behavior similar to that of semiconductors [6٨].

Table (3.2): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for pure polymer (I).

Temperature (K)	1000/T	Resistivity (ρ) ohm	Conductivity(σ) $S.cm^{-1}$	lnσ
298	3.355705	3.51856E+11	2.84208E-12	-26.5865
303	3.30033	3.30939E+11	3.0217E-12	-26.5252
308	3.246753	2.94685E+11	3.39346E-12	-26.4092
313	3.194888	2.65867E+11	3.76128E-12	-26.3063
318	3.144654	2.3612E+11	4.23514E-12	-26.1876
323	3.095975	2.15204E+11	4.64676E-12	-26.0949
328	3.04878	1.91034E+11	5.23467E-12	-25.9757
333	3.003003	1.67794E+11	5.9597E-12	-25.846
338	2.95858	1.413E+11	7.07714E-12	-25.6742
343	2.915452	1.2875E+11	7.76697E-12	-25.5811
348	2.873563	98073355263	1.01964E-11	-25.309
353	2.832861	88777302632	1.12641E-11	-25.2094
358	2.793296	84594078947	1.18212E-11	-25.1611
363	2.754821	80968618421	1.23505E-11	-25.1173
368	2.717391	79481250000	1.25816E-11	-25.0988
373	2.680965	78086842105	1.28063E-11	-25.0811

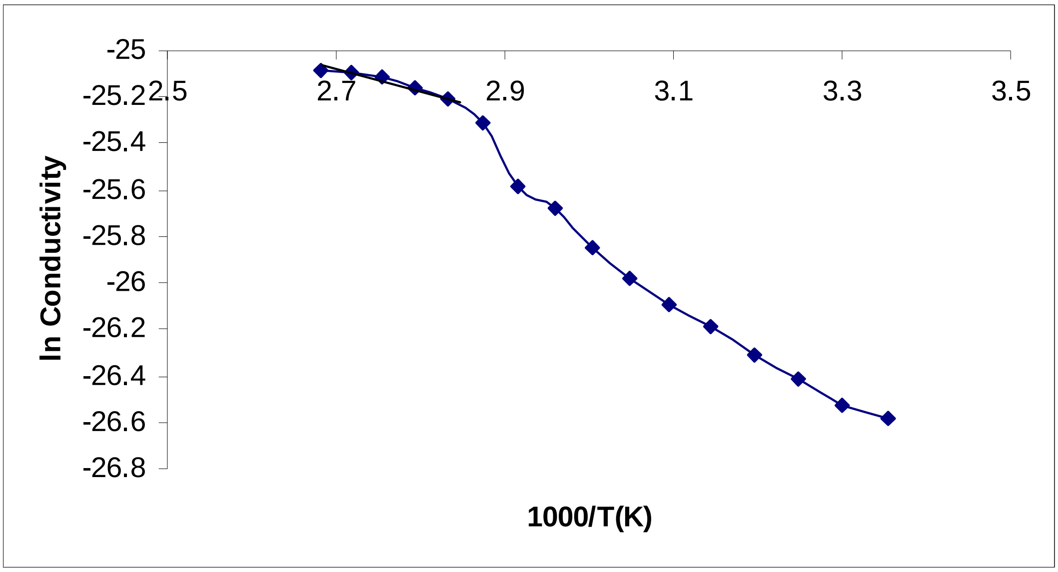


Figure (3-6): Plot of conductivity vs 1000/T for pure polymer (I).

Table (3.3): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for polymer (I) doped with $CuCl_2$

Temperature (K)	1000/T	Resistivity (ρ) ohm	Conductivity(σ) $S.cm^{-1}$	lnσ
298	3.355705	41286094	2.42212E-08	-17.536
303	3.30033	35722406	2.79936E-08	-17.3913
308	3.246753	30997688	3.22605E-08	-17.2494
313	3.194888	21857344	4.57512E-08	-16.9
318	3.144654	15896250	6.29079E-08	-16.5816
323	3.095975	12717000	7.86349E-08	-16.3585
328	3.04878	8478000	1.17952E-07	-15.953
333	3.003003	6446813	1.55115E-07	-15.6791
338	2.95858	4415625	2.26469E-07	-15.3007
343	2.915452	3488344	2.86669E-07	-15.0649
348	2.873563	3488344	2.86669E-07	-15.0649
353	2.832861	2870156	3.48413E-07	-14.8699
358	2.793296	2296125	4.35516E-07	-14.6467
363	2.754821	1192219	8.38772E-07	-13.9913
368	2.717391	794812.5	1.25816E-6	-13.0856
373	2.680965	154546.9	6.47053E-6	-11.9483

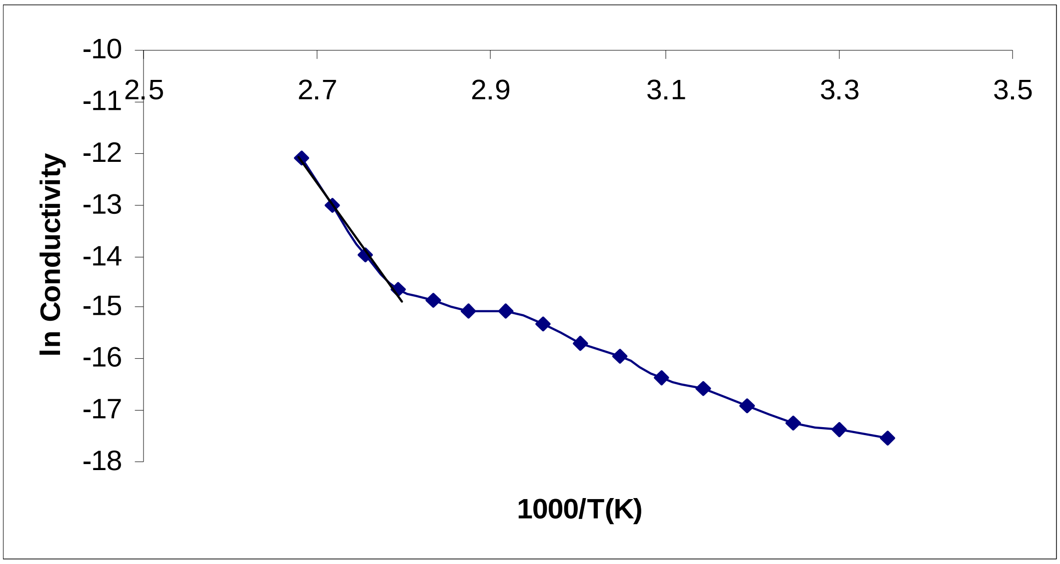


Figure (3-7): Plot of conductivity vs 1000/T for polymer (I) doped with $CuCl_2$

Table (3.4): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for polymer (I) doped with $NiCl_2$

Temperature (K)	1000/T	Resistivity ohm	Conductivity Sm.cm^{-1}	lnσ
298	3.355705	387733929	2.57909E-09	-19.7758
303	3.30033	299000893	3.34447E-09	-19.516
308	3.246753	153916071	6.49705E-09	-18.8519
313	3.194888	96723214	1.03388E-08	-18.3874
318	3.144654	55090179	1.81521E-08	-17.8245
323	3.095975	30699107	3.25742E-08	-17.2397
328	3.04878	16400893	6.09723E-08	-16.6128
333	3.003003	8831250	1.13234E-07	-15.9938
338	2.95858	4205357.1	2.37792E-07	-15.2519
343	2.915452	1850357.1	5.40436E-07	-14.4309
348	2.873563	1240580.4	8.06074E-07	-14.0311
353	2.832861	1093392.9	9.14584E-07	-13.9048
358	2.793296	832660.71	1.20097E-06	-13.6324
363	2.754821	601366.07	1.66288E-06	-13.307
368	2.717391	264937.5	3.77448E-06	-12.4872
373	2.680965	100928.57	9.908E-06	-11.5222

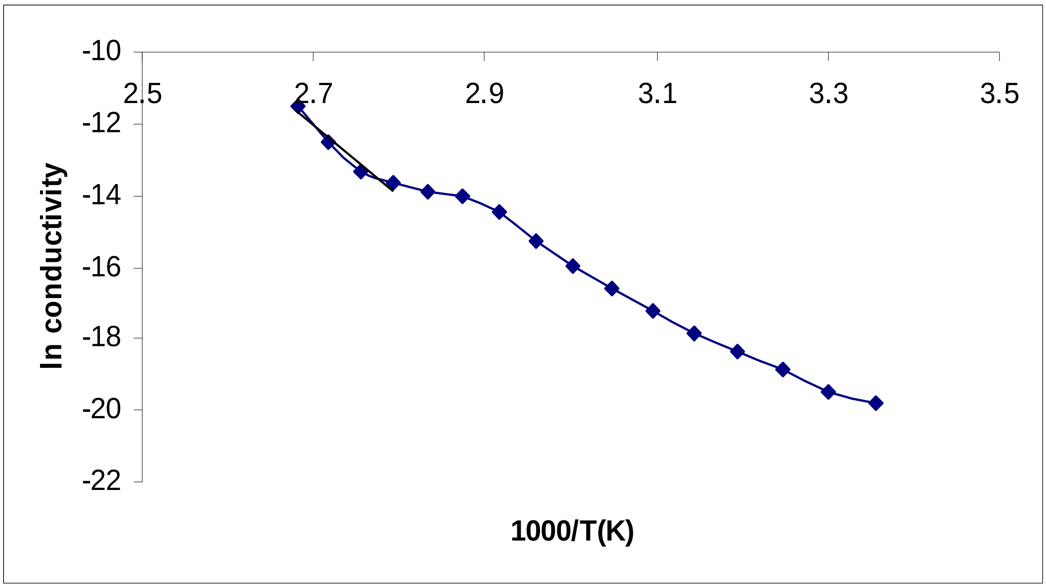


Figure (3-8): Plot of conductivity vs 1000/T for polymer (I) doped with $NiCl_2$

Table (3.5): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for polymer (I) doped with $FeCl_2$

Temperature (K)	1000/T	Resistivity ohm	Conductivity, $Sm.cm^{-1}$	lnσ
298	3.355705	63988714	1.56E-08	-17.9742
303	3.30033	59043214	1.69E-08	-17.8938
308	3.246753	50565214	1.98E-08	-17.7388
313	3.194888	46578536	2.15E-08	-17.6567
318	3.144654	43197429	2.31E-08	-17.5813
323	3.095975	27805821	3.6E-08	-17.1408
328	3.04878	22052893	4.53E-08	-16.909
333	3.003003	10042393	9.96E-08	-16.1223
338	2.95858	5954785.7	1.68E-07	-15.5997
343	2.915452	4693178.6	2.13E-07	-15.3616
348	2.873563	4491321.4	2.23E-07	-15.3177
353	2.832861	3734357.1	2.68E-07	-15.1331
358	2.793296	3633428.6	2.75E-07	-15.1057
363	2.754821	3431571.4	2.91E-07	-15.0485
368	2.717391	3078321.4	3.25E-07	-14.9399
373	2.680965	2624142.9	3.81E-07	-14.7803

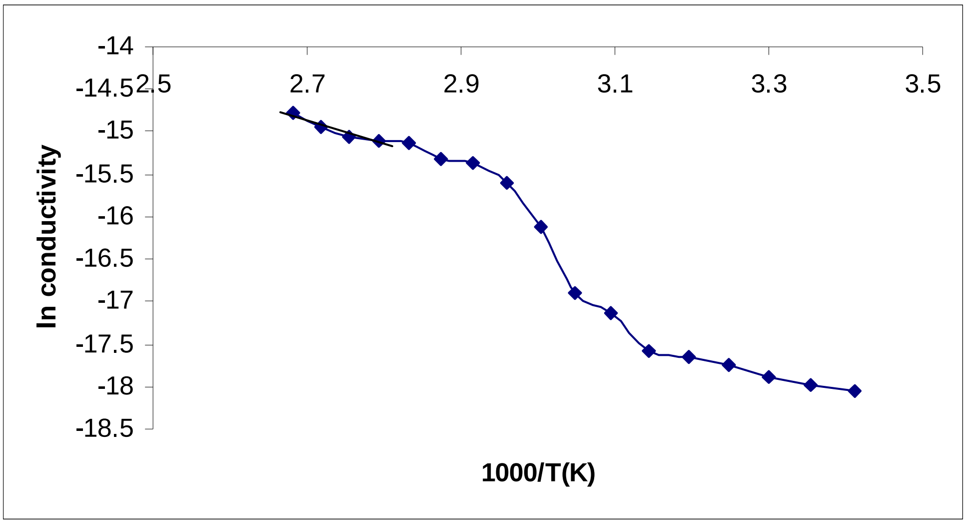


Figure (3-9): Plot of conductivity vs 1000/T for polymer (I)doped with $FeCl_2$

Table (3.6): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for polymer (I) doped with $LiClO_4$

Temperature (K)	1000/T	Resistivity(ρ) ohm	Conductivity(σ) Sm.cm^{-1}	lnσ
298	3.355705	706500	1.41543E-06	-13.4681
303	3.30033	694725	1.43942E-06	-13.4513
308	3.246753	557350	1.7942E-06	-13.2309
313	3.194888	431750	2.31616E-06	-12.9756
318	3.144654	380725	2.62657E-06	-12.8498
323	3.095975	365025	2.73954E-06	-12.8077
328	3.04878	317925	3.1454E-06	-12.6696
333	3.003003	298300	3.35233E-06	-12.6059
338	2.95858	239425	4.17667E-06	-12.386
343	2.915452	227650	4.39271E-06	-12.3356
348	2.873563	208025	4.80711E-06	-12.2454
353	2.832861	176625	5.66171E-06	-12.0818
358	2.793296	149150	6.70466E-06	-11.9127
363	2.754821	113825	8.78542E-06	-11.6424
368	2.717391	86350	1.15808E-05	-11.3662
373	2.680965	66725	1.49869E-05	-11.1083

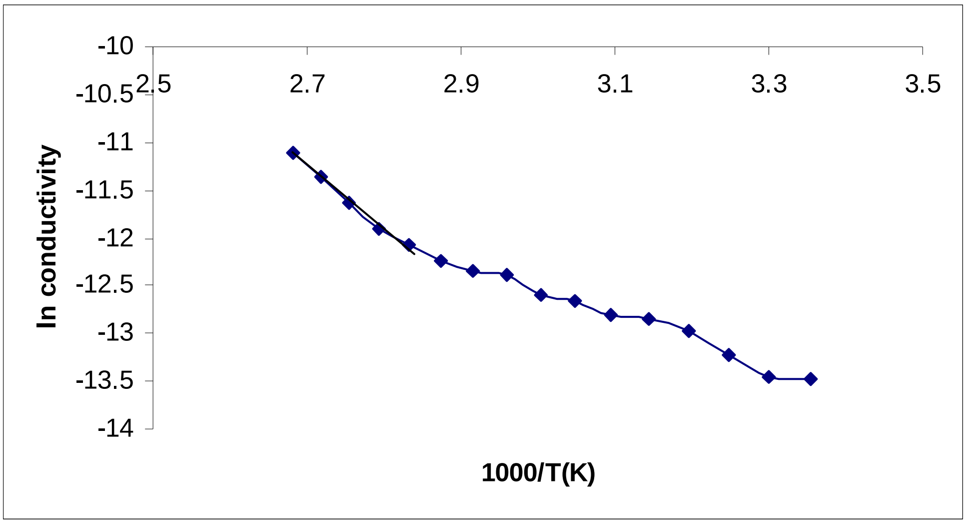


Figure (3-10): Plot of conductivity vs 1000/T for polymer (I)doped with $LiClO_4$

Table (3.7): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for pure polymer (II)

Temperature (K)	1000/T	Resistivity(ρ) ohm	Conductivity(σ) $S.cm^{-1}$	lnσ
298	3.355705	7.02463E+11	1.42356E-12	-27.2779
303	3.30033	3.80501E+11	2.62812E-12	-26.6648
308	3.246753	1.6956E+11	5.89762E-12	-25.8565
313	3.194888	66612857143	1.50121E-11	-24.9222
318	3.144654	25736785714	3.88549E-11	-23.9712
323	3.095975	13120714286	7.62154E-11	-23.2975
328	3.04878	10597500000	9.43619E-11	-23.0839
333	3.003003	8074285714	1.2385E-10	-22.812
338	2.95858	5551071429	1.80145E-10	-22.4373
343	2.915452	4087607143	2.44642E-10	-22.1312
348	2.873563	2472750000	4.04408E-10	-21.6286
353	2.832861	1564392857	6.39226E-10	-21.1708
358	2.793296	656035714.3	1.52431E-09	-20.3017
363	2.754821	423900000	2.35905E-09	-19.865
368	2.717391	242228571.4	4.12833E-09	-19.3054
373	2.680965	181671428.6	5.50444E-09	-19.0177

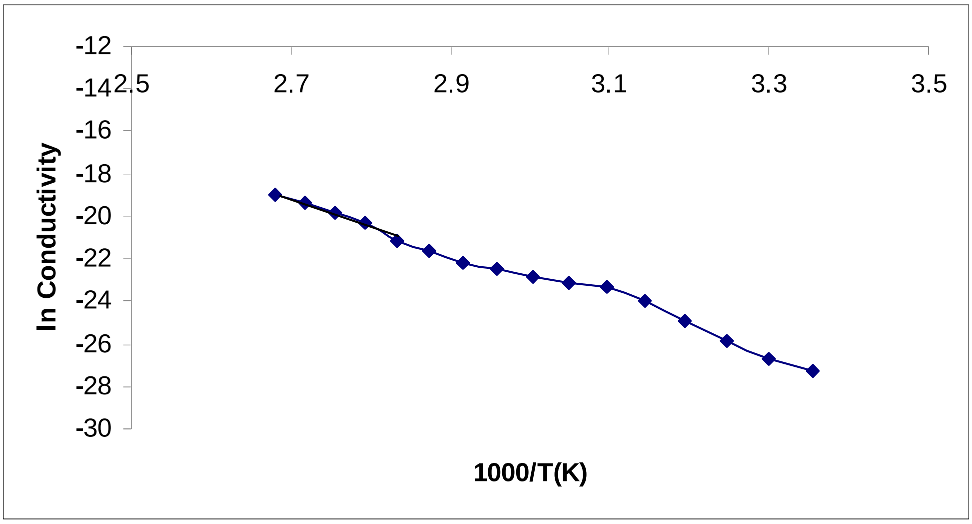


Figure (3-11): Plot of conductivity vs 1000/T for pure polymer (II)

Table (3.8): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for polymer (II) doped with $CuCl_2$

Temperature (K)	1000/T	Resistivity(ρ) ohm	Conductivity(σ) $S.cm^{-1}$	ln σ
298	3.355705	9442373	1.05906E-07	-16.0607
303	3.30033	7571384	1.32076E-07	-15.8399
308	3.246753	5339021	1.873E-07	-15.4906
313	3.194888	3042542	3.28673E-07	-14.9282
318	3.144654	1573729	6.35434E-07	-14.269
323	3.095975	786864.4	1.27087E-06	-13.5758
328	3.04878	562462.3	1.7779E-06	-13.2401
333	3.003003	542645	1.84283E-06	-13.2042
338	2.95858	525742	1.90207E-06	-13.1726
343	2.915452	431901.1	2.31534E-06	-12.976
348	2.873563	408003.8	2.45096E-06	-12.919
353	2.832861	375363.5	2.66408E-06	-12.8357
358	2.793296	301339.9	3.31851E-06	-12.616
363	2.754821	212162	4.71338E-06	-12.2651
368	2.717391	146298.5	6.83534E-06	-11.8934
373	2.680965	69943.5	1.42973E-05	-11.1554

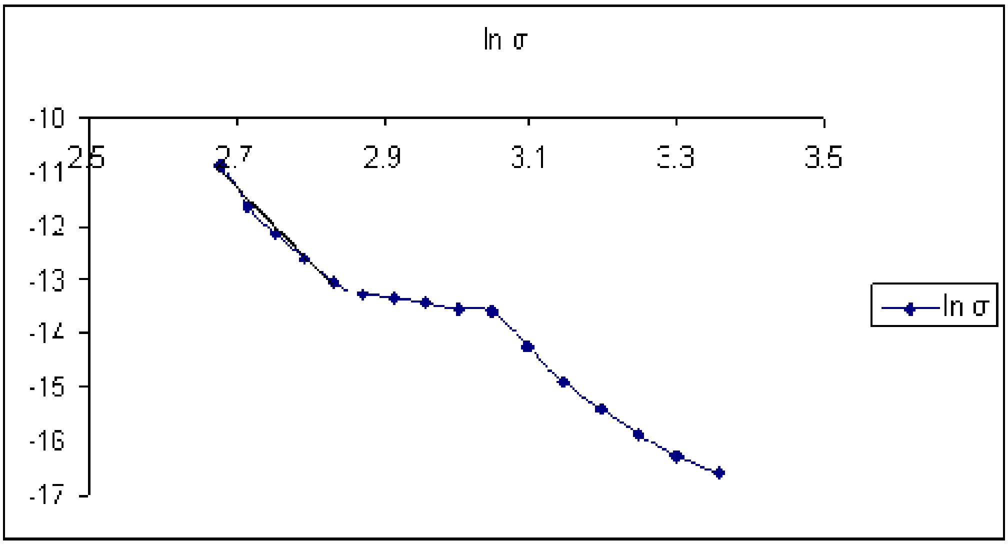


Figure (3-12): Plot of conductivity vs 1000/T for polymer (II)doped with $CuCl_2$

Table (3.9): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for polymer (II) doped with $FeCl_2$

Temperature (K)	1000/T	Resistivity(ρ) ohm	Conductivity(σ) $S.cm^{-1}$	ln σ
298	3.355705	299281250	3.34134E-09	-19.5169
303	3.30033	199684375	5.0079E-09	-19.1122
308	3.246753	118731250	8.42238E-09	-18.5924
313	3.194888	70159375	1.42533E-08	-18.0663
318	3.144654	42831563	2.33473E-08	-17.5728
323	3.095975	23157500	4.31826E-08	-16.9578
328	3.04878	12314688	8.12038E-08	-16.3263
333	3.003003	6034687.5	1.65709E-07	-15.613
338	2.95858	3758187.5	2.66086E-07	-15.1394
343	2.915452	2462937.5	4.06019E-07	-14.7169
348	2.873563	2031187.5	4.92323E-07	-14.5241
353	2.832861	1780968.8	5.61492E-07	-14.3927
358	2.793296	1413000	7.07714E-07	-14.1612
363	2.754821	956718.75	1.04524E-06	-13.7713
368	2.717391	436656.25	2.29013E-06	-12.9869
373	2.680965	181531.25	5.50869E-06	-12.1092

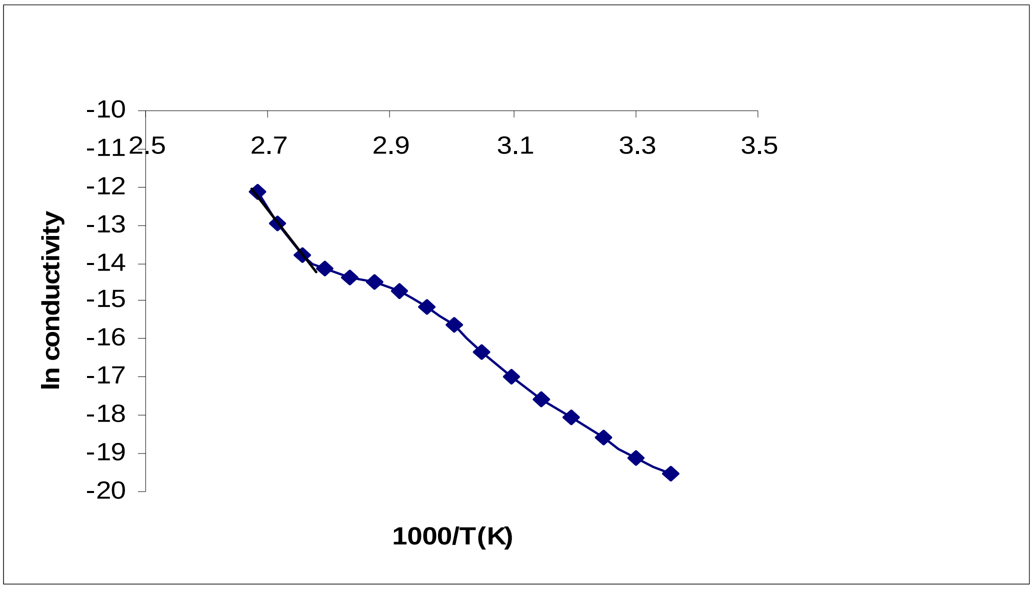


Figure (3-13): Plot of conductivity vs 1000/T for polymer (II) doped with $FeCl_2$

Table (3.10): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for polymer (II) doped with $NiCl_2$

Temperature (K)	1000/T	Resistivity(ρ) Ohm	Conductivity(σ) Scm^{-1}	ln σ
298	3.355705	15849770	6.30924E-08	-16.5787
303	3.30033	11573586	8.64036E-08	-16.2642
308	3.246753	7529803	1.32806E-07	-15.8344
313	3.194888	4880428	2.049E-07	-15.4007
318	3.144654	2881776	3.47008E-07	-14.8739
323	3.095975	1533849	6.51955E-07	-14.2433
328	3.04878	791558.9	1.26333E-06	-13.5818
333	3.003003	751585.9	1.33052E-06	-13.5299
338	2.95858	686978.3	1.45565E-06	-13.4401
343	2.915452	632131.6	1.58195E-06	-13.3569
348	2.873563	569383.2	1.75629E-06	-13.2523
353	2.832861	457365.8	2.18643E-06	-13.0332
358	2.793296	304910.5	3.27965E-06	-12.6278
363	2.754821	191963.5	5.20932E-06	-12.1651
368	2.717391	130609.5	7.65641E-06	-11.78
373	2.680965	102721.4	9.73507E-06	-11.5398

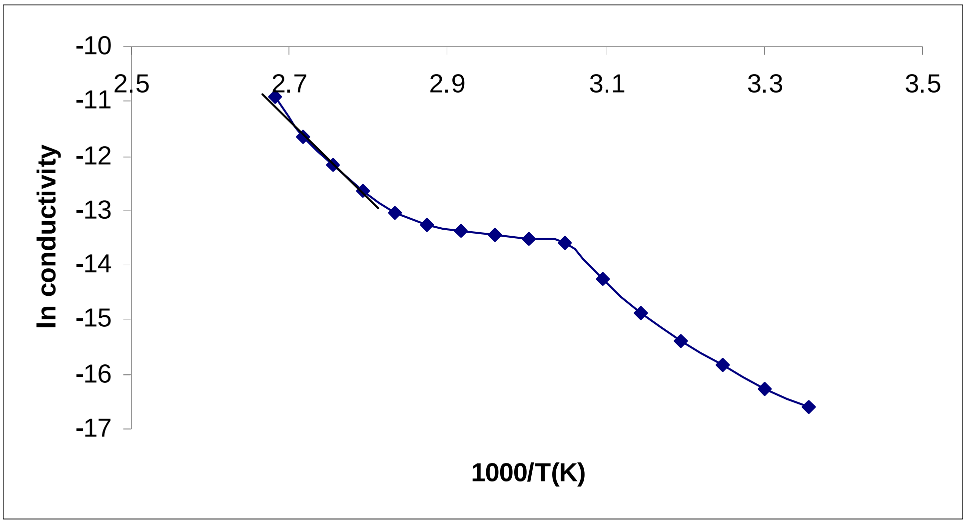


Figure (3-14): Plot of conductivity vs 1000/T for polymer (II)doped with $NiCl_2$

Table (3.11): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for polymer (II) doped with $LiClO_4$

Temperature (K)	1000/T	Resistivity(ρ) ohm	Conductivity(σ) $S.cm^{-1}$	lnσ
298	3.355705	18465341	5.41555E-08	-16.7314
303	3.30033	15789205	6.33344E-08	-16.5748
308	3.246753	12684886	7.8834E-08	-16.3559
313	3.194888	9794659	1.02096E-07	-16.0973
318	3.144654	7653750	1.30655E-07	-15.8507
323	3.095975	6101591	1.63892E-07	-15.6241
328	3.04878	5073955	1.97085E-07	-15.4396
333	3.003003	4410273	2.26743E-07	-15.2994
338	2.95858	3784057	2.64267E-07	-15.1463
343	2.915452	2692193	3.71444E-07	-14.8059
348	2.873563	1482580	6.745E-07	-14.2093
353	2.832861	155215.9	6.44264E-06	-11.9526
358	2.793296	81889.77	1.22115E-05	-11.3131
363	2.754821	61015.91	1.63892E-05	-11.0189
368	2.717391	49776.14	2.00899E-05	-10.8153
373	2.680965	44423.86	2.25104E-05	-10.7015

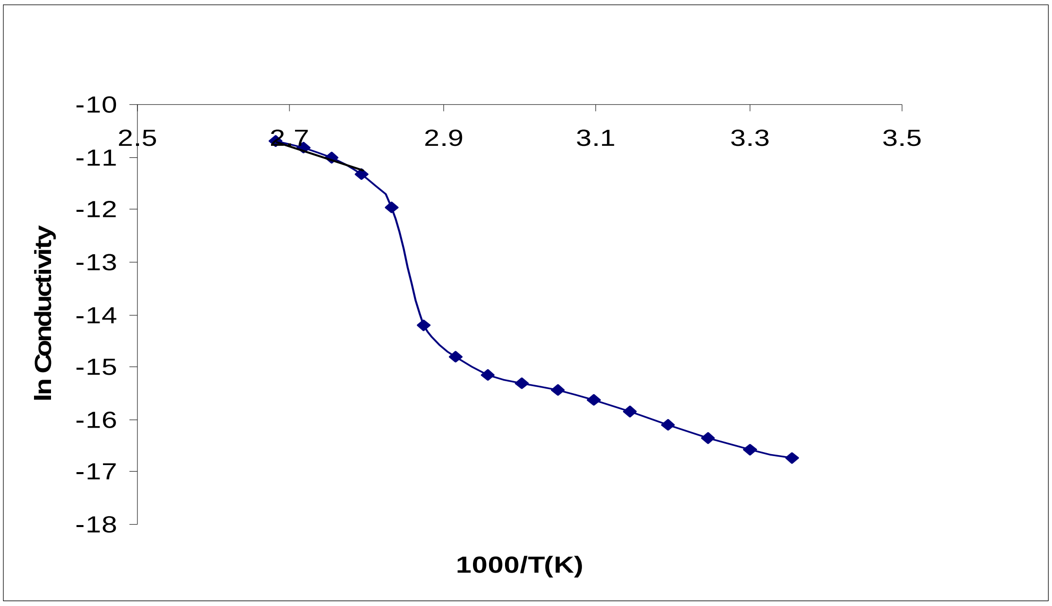


Figure (3-15): Plot of conductivity vs 1000/T for polymer (II)doped with $LiClO_4$

Table (3.12): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for pure polymer (III).

Temperature (K)	1000/T	Resistivity(ρ) ohm	Conductivity(σ) S.cm^{-1}	lnσ
298	3.355705	7.79E+10	1.28437E-11	-25.0782
303	3.30033	6.49E+10	1.54124E-11	-24.8958
308	3.246753	4.65E+10	2.15057E-11	-24.5627
313	3.194888	3.17E+10	3.15254E-11	-24.1802
318	3.144654	2.05E+10	4.86709E-11	-23.7459
323	3.095975	1.41E+10	7.11343E-11	-23.3665
328	3.04878	1.05E+10	9.56634E-11	-23.0702
333	3.003003	7.57E+09	1.32107E-10	-22.7474
338	2.95858	6.13E+09	1.63191E-10	-22.5361
343	2.915452	5.05E+09	1.9816E-10	-22.3419
348	2.873563	3.68E+09	2.71984E-10	-22.0253
353	2.832861	2.83E+09	3.53857E-10	-21.7621
358	2.793296	1.24E+09	8.04127E-10	-20.9413
363	2.754821	5.41E+08	1.84949E-09	-20.1084
368	2.717391	2.92E+08	3.42499E-09	-19.4922
373	2.680965	1.48E+08	6.76644E-09	-18.8113

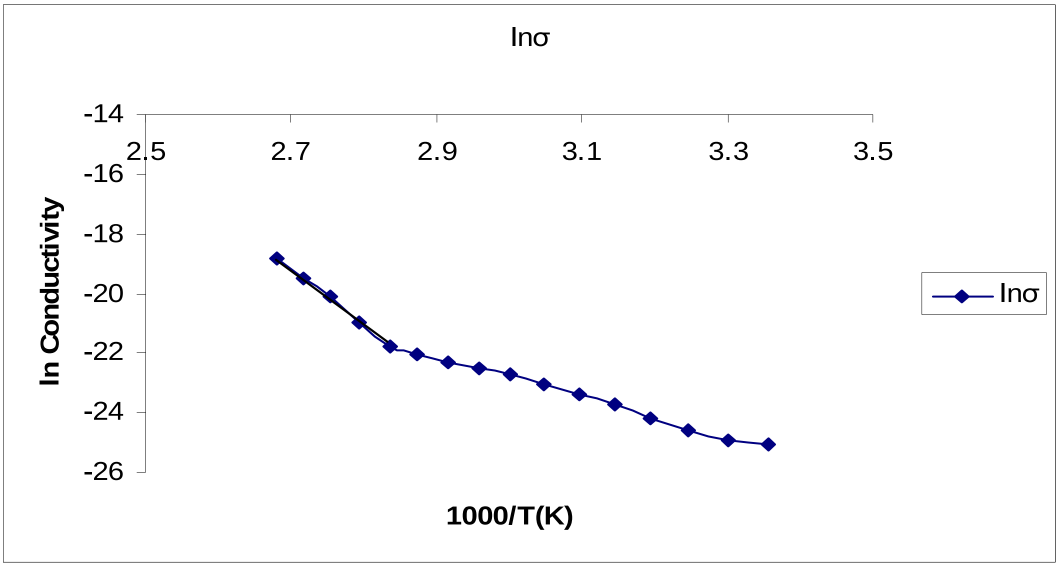


Figure (3-16): Plot of conductivity vs 1000/T for pure polymer (III)

Table (3.13): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for polymer (III) doped with $CuCl_2$

Temperature (K)	1000/T	Resistivity(ρ) ohm	Conductivity(σ) $S.cm^{-1}$	lnσ
298	3.355705	373856250	2.67482E-09	-19.7394
303	3.30033	276221875	3.62028E-09	-19.4367
308	3.246753	180550000	5.53863E-09	-19.0115
313	3.194888	115296875	8.67326E-09	-18.563
318	3.144654	74084375	1.34981E-08	-18.1207
323	3.095975	49062500	2.03822E-08	-17.7086
328	3.04878	31449063	3.17975E-08	-17.2639
333	3.003003	18447500	5.42079E-08	-16.7304
338	2.95858	8242500	1.21322E-07	-15.9248
343	2.915452	2222531.3	4.49937E-07	-14.6142
348	2.873563	1481687.5	6.74906E-07	-14.2087
353	2.832861	1339406.3	7.46599E-07	-14.1077
358	2.793296	932187.5	1.07275E-06	-13.7453
363	2.754821	858593.75	1.1647E-06	-13.6631
368	2.717391	785000	1.27389E-06	-13.5734
373	2.680965	328718.75	3.04211E-06	-12.703

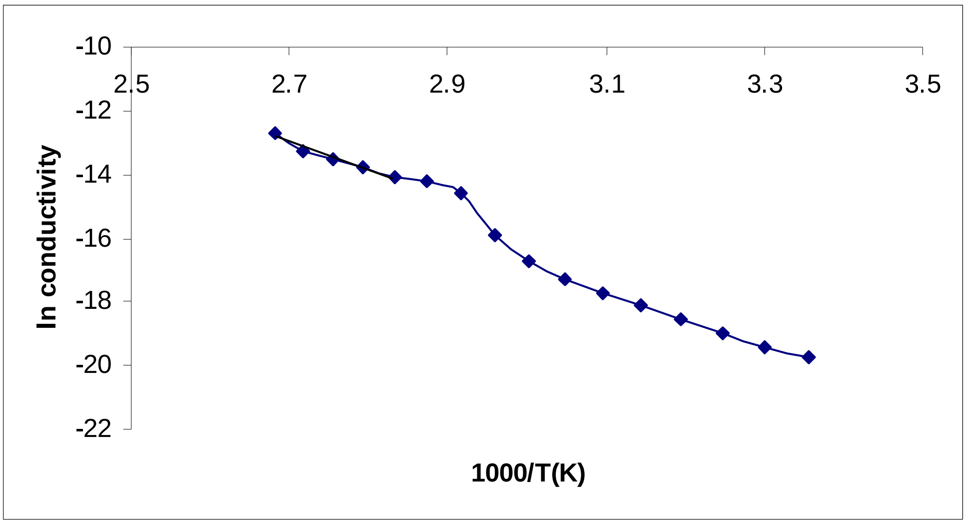


Figure (3-17): Plot of conductivity vs 1000/T for polymer (III) doped with $CuCl_2$

Table (3.14): Values of Resistance, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for polymer (III) doped with $NiCl_2$

Temperature (K)	1000/T	Resistivity(ρ) ohm	Conductivity(σ) $S.cm^{-1}$	lnσ
298	3.355705	406891667	2.45766E-09	-19.8241
303	3.30033	273441667	3.65709E-09	-19.4266
308	3.246753	162233333	6.16396E-09	-18.9045
313	3.194888	87658333	1.14079E-08	-18.289
318	3.144654	45268333	2.20905E-08	-17.6281
323	3.095975	22568750	4.43091E-08	-16.9321
328	3.04878	10008750	9.99126E-08	-16.119
333	3.003003	4324041.7	2.31265E-07	-15.2797
338	2.95858	2355000	4.24628E-07	-14.6721
343	2.915452	1596166.7	6.26501E-07	-14.2831
348	2.873563	1144791.7	8.73521E-07	-13.9507
353	2.832861	1066291.7	9.3783E-07	-13.8797
358	2.793296	752291.67	1.32927E-06	-13.5309
363	2.754821	719583.33	1.38969E-06	-13.4864
368	2.717391	680333.33	1.46987E-06	-13.4303
373	2.680965	660708.33	1.51353E-06	-13.4011

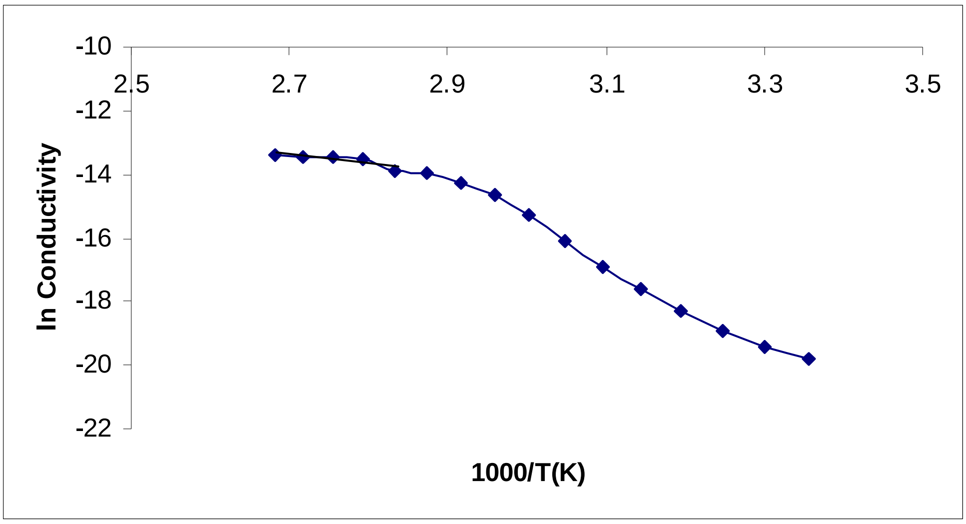


Figure (3-18): Plot of conductivity vs 1000/T for polymer (III)doped with $NiCl_2$

Table (3.15): Values of Resistivity, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for polymer (III) doped with $FeCl_2$

Temperature (K)	1000/T	Resistivity (ρ) ohm	Conductivity(σ) $S.cm^{-1}$	lnσ
298	3.355705	192729044	5.18863E-09	-19.0768
303	3.30033	138183088	7.23678E-09	-18.7441
308	3.246753	97663235	1.02393E-08	-18.397
313	3.194888	66494118	1.50389E-08	-18.0126
318	3.144654	43636765	2.29165E-08	-17.5914
323	3.095975	26493750	3.77448E-08	-17.0924
328	3.04878	13039081	7.66925E-08	-16.3835
333	3.003003	6763698.5	1.47848E-07	-15.7271
338	2.95858	4368871.3	2.28892E-07	-15.29
343	2.915452	3615617.6	2.76578E-07	-15.1008
348	2.873563	3262367.6	3.06526E-07	-14.998
353	2.832861	2768856.6	3.6116E-07	-14.8339
358	2.793296	2379242.6	4.20302E-07	-14.6823
363	2.754821	2311709.6	4.3258E-07	-14.6535
368	2.717391	2098720.6	4.76481E-07	-14.5568
373	2.680965	2005213.2	4.987E-07	-14.5113

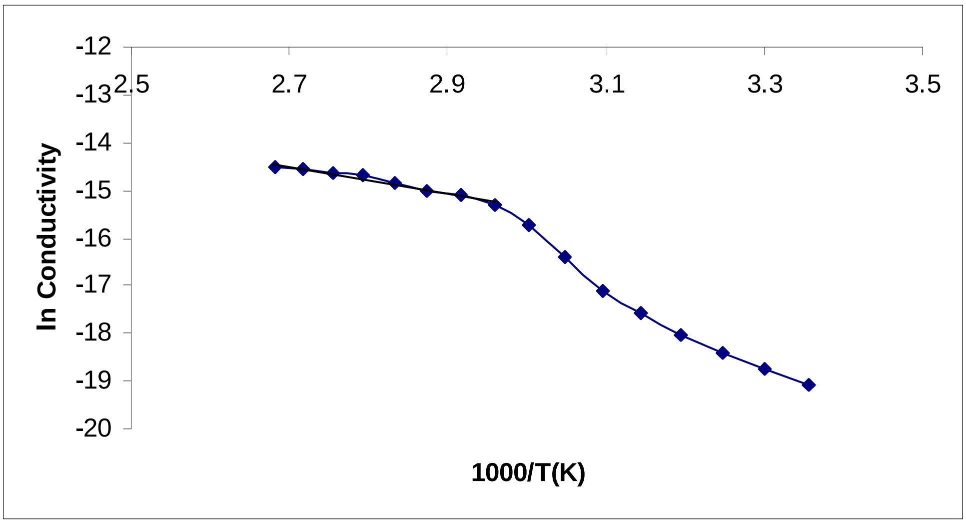


Figure (3-19): Plot of conductivity vs 1000/T for polymer (III)doped with $FeCl_2$

Table (3.16): Values of Resistivity, Conductivities and the Corresponding Temperatures, ln δ and 1000/T for polymer (III) doped with $LiClO_4$

Temperature (K)	1000/T	Resistivity(ρ) ohm	Conductivity(σ) $S.cm^{-1}$	lnσ
298	3.355705	48263143	2.07197E-08	-17.6922
303	3.30033	25714286	3.88889E-08	-17.0626
308	3.246753	11428571	8.75E-08	-16.2516
313	3.194888	4754571	2.10324E-07	-15.3746
318	3.144654	3394571	2.94588E-07	-15.0377
323	3.095975	2088643	4.7878E-07	-14.552
328	3.04878	1535111	6.51419E-07	-14.2441
333	3.003003	1252126	7.98642E-07	-14.0404
338	2.95858	1028571	9.72222E-07	-13.8437
343	2.915452	766640	1.30439E-06	-13.5498
348	2.873563	650082.9	1.53827E-06	-13.3849
353	2.832861	494445.7	2.02247E-06	-13.1112
358	2.793296	384825.7	2.59858E-06	-12.8605
363	2.754821	318731.4	3.13744E-06	-12.6721
368	2.717391	290745.7	3.43943E-06	-12.5802
373	2.680965	262311.4	3.81226E-06	-12.4773

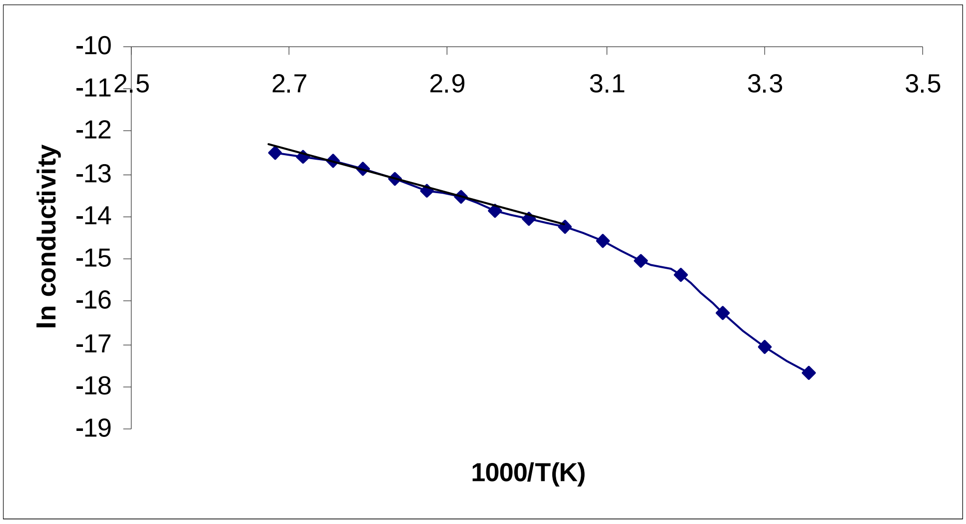


Figure (3-20): Plot of conductivity vs 1000/T for polymer (III) doped with $LiClO_4$

Looking at the prepared polymers and their structure, we notice that all polymers contains nitrogen and oxygen atoms in different percents, the presence of these atoms in the polymer chains enhance the interaction between the polymer and the dopants and consequently enhance the conductivity of the polymer .

The expect effect of the presence of high percent of nitrogen and oxygen to increase the conductivity was enhanced after measuring the conductivity of the polymers in the pure stat, polymer III showed higher conductivity than polymer II and I due to high percent content of nitrogen atoms. (see tables (3.2), (3.7) and (3.12) and figures (3.6), (3.11) and (3.16)).

This effect in doped state is not like in pure state, in doped state the response of polymer to temperature is less for polymer III comparing with polymers I and II and that because of the segmental motion of the chains is lower than the other polymers and also the length of the chains in polymers I and II is greater than polymer III. As reported by J. Xi, X. Tang [٦٩] the increase in the length of the chains and their motions could increase the conductivity of the polymer.

Now by back to the result obtained for polymers in the pure state is compete with the result obtained by X-Ray in which the curve tend to be straight line as the property of crystalline materials.

3.3.1.4 Activation energy calculation

Activation energy is defined as the amount of energy required to make an electron excitement from the valance band to conduction band.

The activation energy of the polymers in the pure and doped state is calculated using the slop method.

Table (3.17) the values of activation energy for polymers in both pure and doped state

Dopant	**Activation energy e.v.**		
	Polymer I	**Polymer II**	**Polymer III**
pure	**0.0228**	**0.0101**	**0.0084**
Cu^{+2}	**0.0033**	**0.0053**	**0.0037**
Ni^{+2}	**0.0063**	**0.0042**	**0.0042**
Fe^{+2}	**0.0084**	**0.0055**	**0.0063**
Li^{+1}	**0.0012**	**0.0024**	**0.0035**

The relationship between conductivity and activation energy is inversely one.

The activation energy is calculated by using Arrhenius equation, the result of activation energy is complying with values of conductivity.

3.3.2 A.C measurements

3.3.2.1 Dielectric constant έ

The variation of dielectric constant (ɛ́) as a function of frequency for the polymers in pure and doped state samples in the case of polar dielectric are shown in figures (3.21), (3.22) and (3.23).

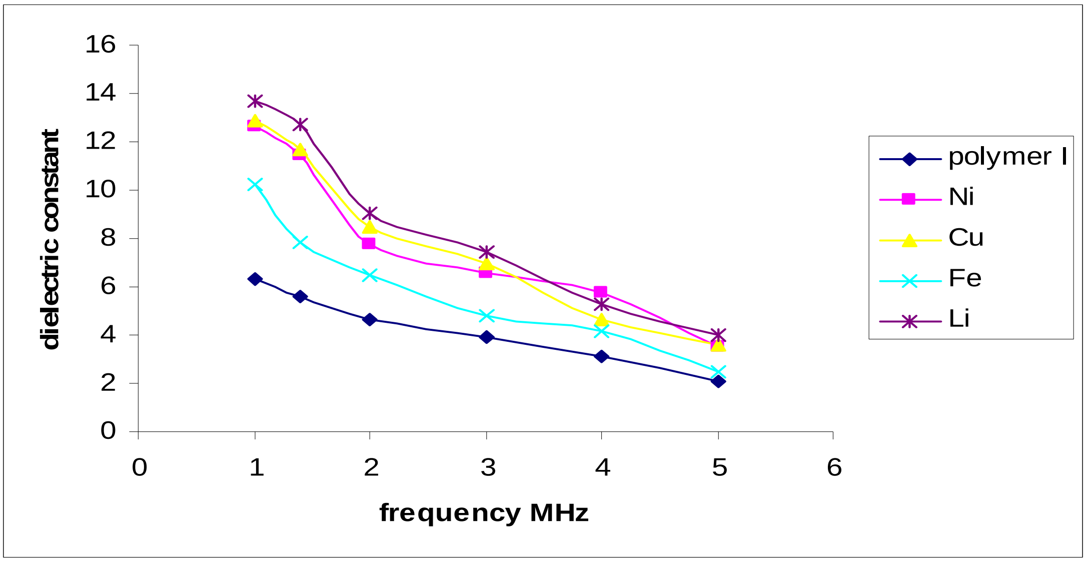


Figure (3.21) effect of frequency on dielectric constant of polymer I in pure and doped state

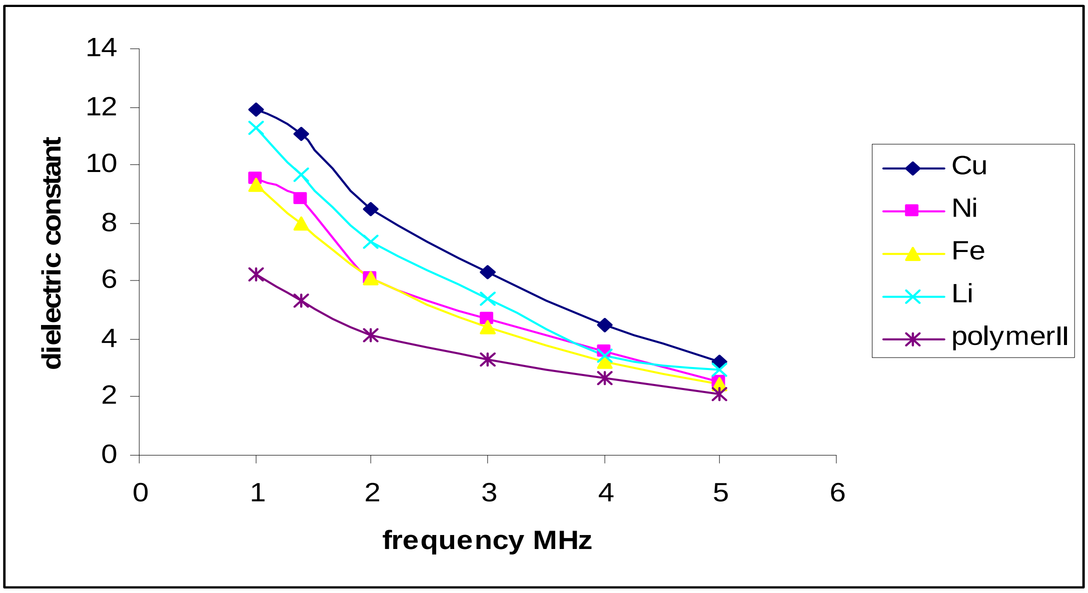


Figure (3.22) effect of frequency on dielectric constant of polymer II in pure and doped state

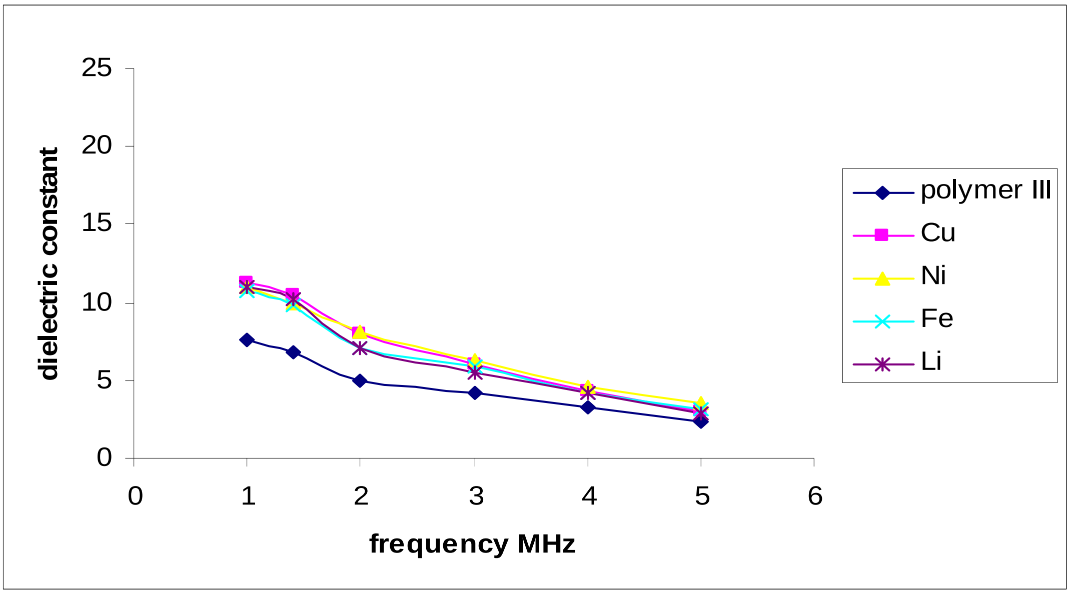


Figure (3.23) effect of frequency on dielectric constant of polymer III in pure and doped state

One could notice that (έ) decrease with increase the frequency, verifying the fact that for polar material, the initial value of (έ) is high but as the frequency of the A.C field is raised, the value of (έ) being droped[7٠].the result characterizing of most dielectric materials as reported in literature [7١].

Chapter Two

Experimental

Chapter two: Experimental

2.1 Chemicals

The chemicals used in this work were listed in table (2-1)

Table(2-1) chemical used in this work

Substance	**source**
Triethanolamine	Fluka
Maleicanhydrid	BDH
Glycerol	Fluka
Cupric chloride	Fluka
Nickle chloride	Fluka
Ferrous chloride	Fluka
Lithium perchlorate	Fluka
Ethanol	BDH
Methanol	Fluka
Benzene	BDH
Carbon tetrachloride	BDH
Dioxane	BDH
Chloroform	Hopkins and Williams
Hexane	Merck

2.2 Preparation of polymer I, II and III[60,61]

In a 100ml round-bottom flask immersed in sand bath and equipped with a thermometer and magnetic stirrer. A mixture of triethanolamine and glycerol was placed. The mixture is stirred for 15 min. and then maleic anhydride was added to the mixture and the temperature raised gradually to 160 ˚C, and maintained for 3 hours. Continued heating at this temperature causes increasing in the viscosity of the solution until crystalline polymer was formed. The final product was washed with warm water and methanol or ethanol for several times.

Table (2.2) content of the prepared polymers

polymer	content
Polymer I	TEA + G + M 0.05 0.15 0.15 mole (TEA:G)=(1:3) (25:75%)
Polymer II	TEA + G + M 0.05 0.05 0.15 mole (TEA:G)=(1:1) (50:50%)
Polymer III	TEA + G + M 0.05 0.00 0.15 mole (TEA:G)=(1:0) (100:0%)

2.4 Solubility

The solubility of the prepared polymers has been examined using different types of solvent like water, methanol, ethanol, dioxane, chloroform, carbon tetra chloride, hexane and benzene and found that all polymers are insoluble and stable in all these solvents.

2.5 X-Ray diffraction

X-ray diffraction pattern were recorded by (X-ray diffractometer Siemens SRS D 500) equipped with copper, (λ=1.542A°). A scan rate of 4.0/min. over the range of 1-60 (2θ) was used for detecting the characteristic diffraction peaks of the prepared polymers in the pure state**.**

2.6 F.T. IR measurement

The infrared spectra were recorded on a ***SHIMADZU*** 8300 Fourier Transform Infrared Spectrophotometer (F.T.IR) by using the (KBr) in the wave number range (4000-400) cm^{-1}.

2.7 Doping of polymers

The polymer was doped with metal salts by adding 0.3 gm (10%w:w) of the salts in ethanol to the polymer (3gm) and then left for seven days to allow the salt to diffuse homogeneously. The doped polymers were dried under vacuum over night.

2.8 Preparation of the Samples

Circular pellet specimens were prepared from the powder of pure and doped polymer samples, under a pressure of 5 ton/cm^2 for 15 minutes. The diameter of the pellet was 2.5 cm and their thickness varied from (2.7-4.9) mm. All the specimens were pressed at 80 °C.

2.9 Preparation of aluminum-electrodes

A coating unit model (Edwards), has been used for deposition of thin aluminum electrodes on both sides of each sample. The shape of electrode is circular and the diameter is (1.5 cm), the deposition of aluminum is done under highly reduced pressure.

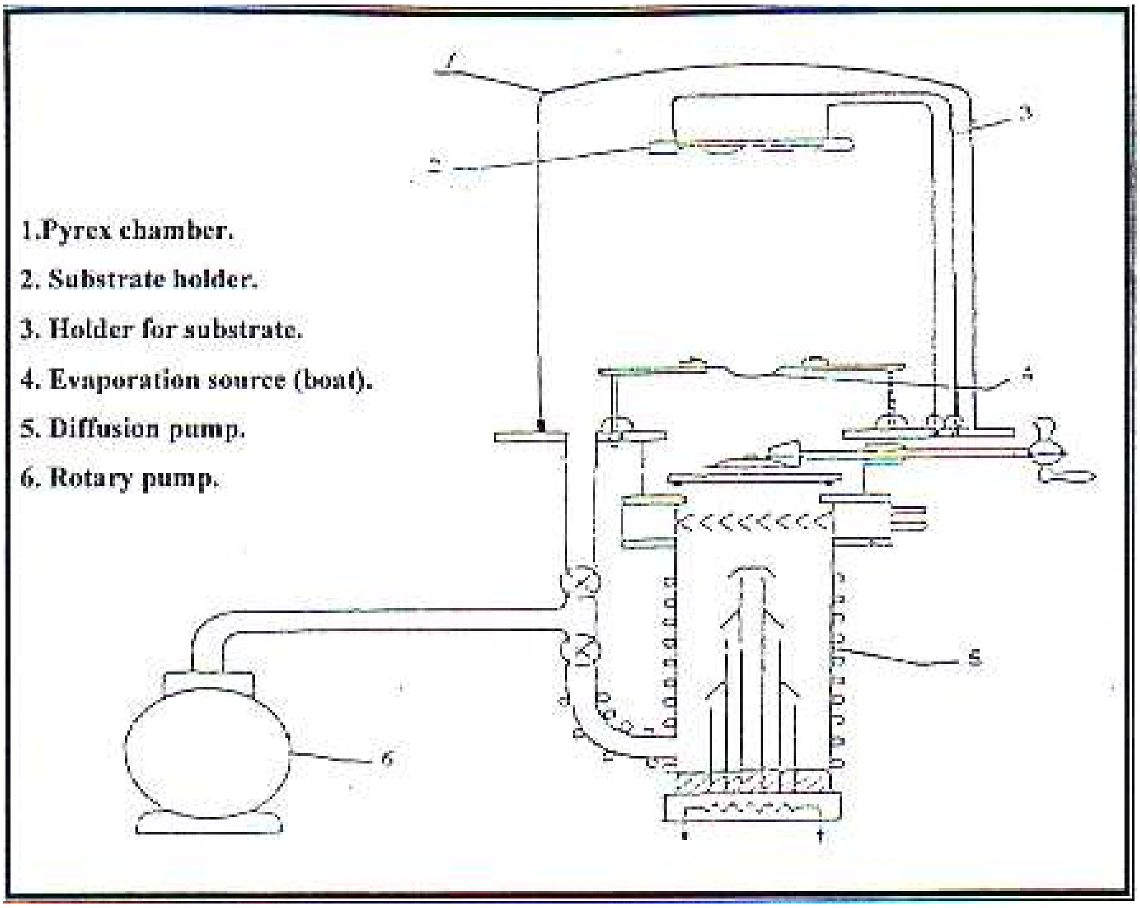


Figure (2.1) simplified diagram for the coating units model (Edwards) [62] .

2.10 Electrical measurements

2.10.1 D.C Electrical measurement

There are different methods for determination of D.C volume resistivety of insulating materials. Three electrode cell or (guard ring electrode method) is used to study the effect of the dopant and the temperature on the volume resistivety of the polymer.

There are two main reasons for an adoption this method in the present work.

The first one is that in guard electrode system the leakage current can be minimized over the surface of the specimen can be collected by the guard electrode and are not included in the measured current (i.e. the surface resistance can be separated from volume resistance considerable extent). The second reason is the ability of this system to decrease the effect of the fringing of the field at the edges.

The volume conductivity (σ_v) is calculated as follow:

$$\rho_v = l/RA \qquad ....(2.1)$$

$$\sigma_v = 1/\rho_v \qquad ....(2.2)$$

where R is the resistance(Ohm).

ρ_v is the volume resistivity

σ_v is the volume conductvity(S cm^{-1}).

l is the thickness of the sample (cm).

A is the guard electrode effective area (cm^2).

The electrode, in this model has a circular area with

$$A=(D/2)^2\pi \qquad .... (2.3)$$

Where D is the electrode diameter

A suitable measuring system is used to study and measure the electrical properties of the polymer in both pure and doped state, the complete system is shown in figure (2.2)

The electrodes were made of copper metal, and two adjustable screws applied a uniform pressure on the specimens. The resistance was measured by using Keithly 614 digital-solid state electrometer.

The test sample is sandwiched between the electrodes and put it in temperature controlled oven (Hereaus electronic). The volume conductivity measurements were performed in the temperature range (298-373K)

2.10.2 A.C electrical measurements

Electrical properties (dielectric constant) have been studied as a function of frequency. All measurements are carried out over a frequency range 1-5MHz.

The guard electrode method has been used to study and measure dopant effect, as shown in figure (2.3) . The high and low specimen's holder terminal are connected to oscilloscope.

The dielectric constant ($\acute{\varepsilon}$) is calculated as follow

$\acute{\varepsilon}= C_p/C_\circ$ ………(2.4)

Where

C_p =capacitance of the material

$C_\circ$ = capacitance of air

$C_\circ = \varepsilon_\circ A/d$

$\varepsilon_\circ = 8.85 * 10^{-12}$

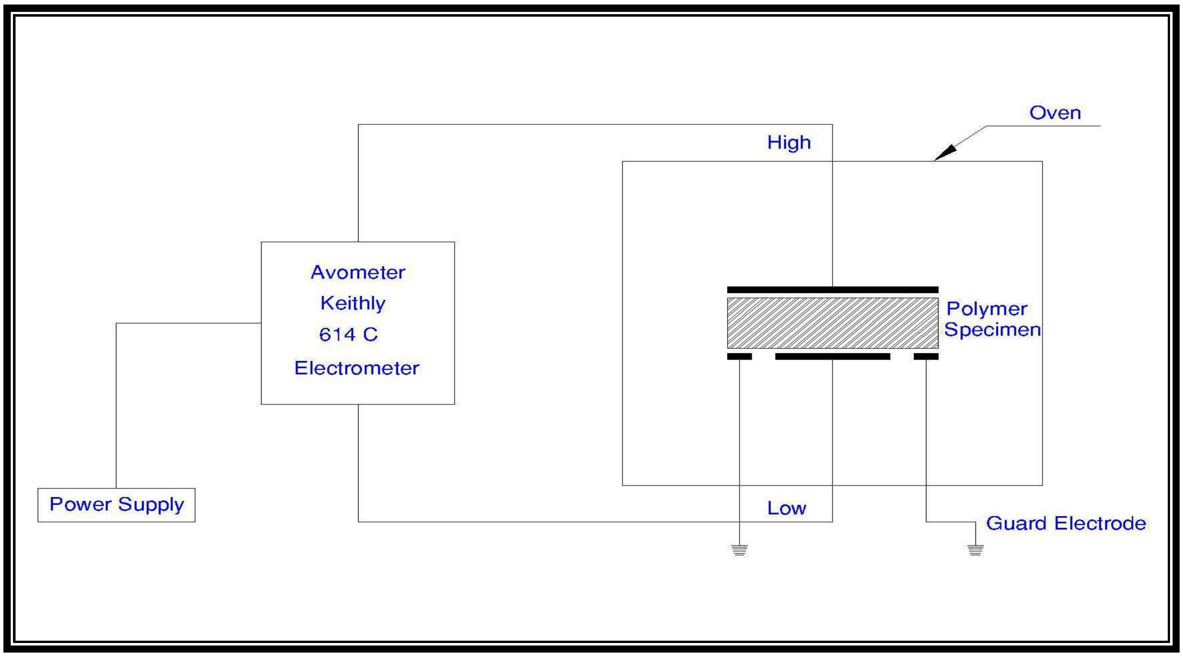


Figure (2.2) **schematic diagram for D.C volume resistivity measurement**

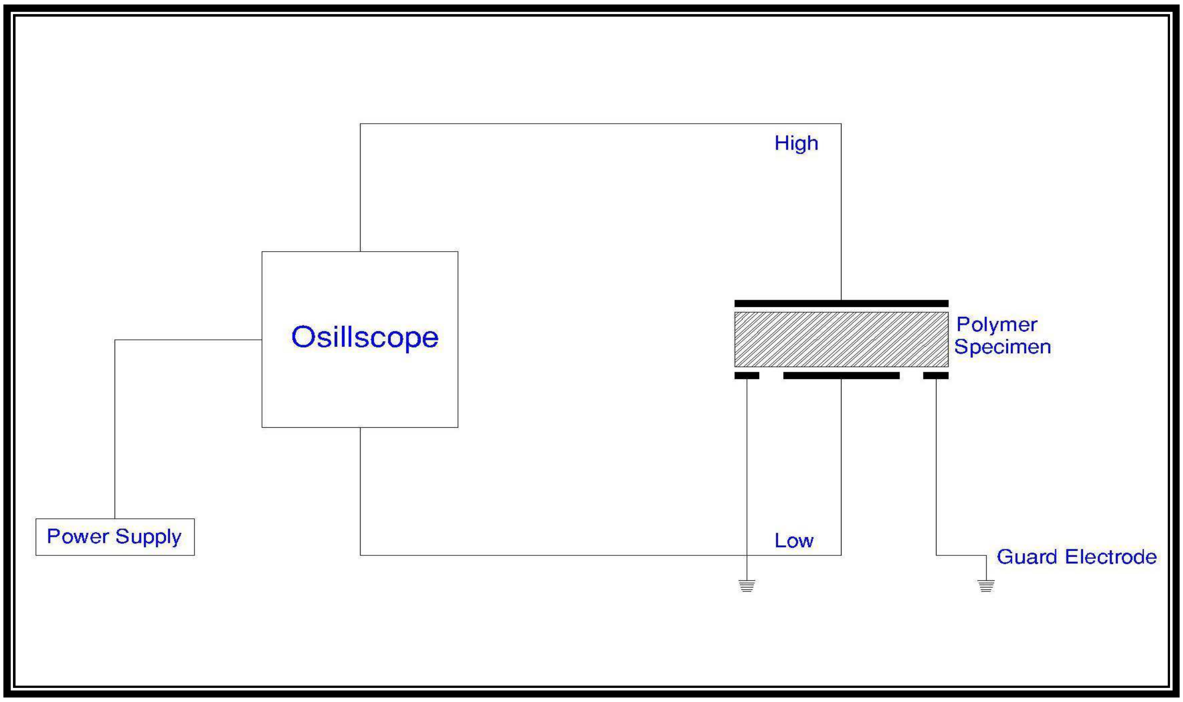


Figure (2.3) schematic diagram for A.C measurement

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Study the electrical conductivity of cross-linked polymers in the pure and doped state

A Thesis submitted to the College of Science Al-Nahrain University in partial fulfillment of the requirements for the Degree of Master of Science in Chemistry.

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